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EMPIRICAL RELATIONSHIPS BETWEEN ATMOSPHERIC NITROGEN DIOXIDE AND ITS PRECURSORS

Environmental Sciences Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

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16. ABSTRACT

Aerometric data were examined to define relationships between atmospheric NO_2 and its precursors. A descriptive and critical analysis of the nationwide data base of NO_2 was carried out, followed by the formulation application and testing of empirical models relating ambient NO_2 changes to NO_x and hydrocarbon (HC) emission controls.

The examination showed that (1) other factors being constant, annual mean and yearly maximum NO_2 are proportional to NO_x input; (2) HC control yields slight-to-moderate reductions in yearly maximum NO_2; (3) HC control yields essentially negligible benefits for annual mean NO_2; and (4) the exact form of the NO_2/precursor relationship may vary somewhat from one location to the next, depending on local conditions.

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ABSTRACT

A two-part study is performed with ambient monitoring data for nitrogen dioxide and its precursors (NO_x and hydrocarbons). Part I deals with a descriptive analysis of the nationwide data base for NO_2; Part II involves empirical models of the NO_2/precursor dependence.

Part I characterizes the statistical properties, geographical patterns, and historical trends of ambient NO_2 concentrations. Included in Part I are a survey and quality check of the nationwide NO_2 data base; a study of statistical distributions for characterizing maximal NO_2 concentrations; a descriptive analysis of present NO_2 air quality for both annual mean and one-hour maximum concentrations; an examination of historical trends in NO_2 air quality; and a study of the relationship between annual mean NO_2 and yearly one-hour maximum NO_2.

Part II formulates, applies, and tests empirical models that indicate the dependence of ambient NO_2 on NO_x and hydrocarbon control. Although the simple empirical models used are subject to uncertainties, the general conclusions of these models agree quite well with smog-chamber results and historical air quality trends. Part II studies lead to the conclusions that (1) with other factors held constant, annual mean and yearly maximum NO_2 are essentially proportional to NO_x input; (2) hydrocarbon control yields slight-to-moderate reductions in yearly maximum NO_2; (3) hydrocarbon control yields very slight, essentially negligible, benefits for annual mean NO_2; and (4) the exact form of the NO_2/precursor relationship may vary somewhat from one location to the next, depending on local conditions.

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1.0 INTRODUCTION AND SUMMARY

The National Ambient Air Quality Standards presently include one standard for nitrogen dioxide, 100 µg/m^3 (0.053 ppm) for the annual mean concentration. In the near future, EPA will revise the "Air Quality Criteria for Nitrogen Oxides." This revision may lead EPA to supplement the long-term standard for NO_2 with a short-term (e.g., one-hour) standard and to consider new control strategies. To support this regulatory program, there is a need for empirical analyses of ambient monitoring data for nitrogen dioxide and its precursors. These analyses should consider both annual mean NO_2 concentrations and maximal short-term NO_2 concentrations.

At least two types of empirical studies are required. The first involves a descriptive analysis of ambient NO_2 concentrations. There is a need to identify regions of the United States that may exceed the annual mean standard and/or a proposed short-term standard for NO_2. Statistical properties of NO_2 frequency distributions and trends in NO_2 air quality should be quantified. Also, data should be assembled for assessing whether the annual standard or a proposed short-term standard is the binding constraint for control strategy formulation.

The second type of study involves empirical modeling of the relationship between NO_2 concentrations and precursors. It is generally agreed that NO_2 concentrations should be proportional to NO_x concentrations with all other factors held constant, but there is substantial uncertainty concerning the impact of hydrocarbon control on ambient NO_2 levels. Empirical modeling techniques, applied to ambient monitoring data, should provide a better understanding of these relationships.

This report is organized in two parts corresponding to the two types of empirical studies. Part I (Chapters 2 through 6) involves a descriptive analysis of the nationwide NO_2 data base; Part II (Chapters 7 through 14) deals with empirical models of the NO_2/precursor relationship. The remainder of this chapter provides a summary of the report.

1.1 SUMMARY OF PART I: DESCRIPTIVE ANALYSIS OF THE NATIONWIDE NO_2 DATA BASE

The objective of Part I is to describe the statistical properties, geographical patterns, and historical trends of ambient NO_2 concentrations. The findings and conclusions of this descriptive analysis are summarized in the paragraphs below. For convenient referencing, the summary is organized according to the order of the chapters (2 through 6).

Data Base Preparation

- As of March 1976, the National Aerometric Data Bank contained 462 station-years of hourly NO_2 data that met EPA's 75% completeness criterion. Most of these data, 302 station-years, are from California. Since 1972, there has been a sharp increase in the number of sites providing complete data sets for NO_2, especially in the number of sites outside California.
- Data quality checks should precede all statistical studies of air monitoring data. In this study, data verification procedures focus on reported yearly one-hour maxima. As a result of the quality check, 42 of the 462 station-years of data are found to require correction. It is remarkable that no errors were uncovered in the California NO_2 data.

Statistical Distributions for Characterizing Maximal Concentrations

- Lognormal distributions which are fit to the entire range of one-hour concentration data overpredict yearly one-hour NO_2 maxima, typically by about 50%. If lognormal distributions are fit to the upper range of the hourly concentration data (e.g., to the arithmetic mean and 99th percentile), the overprediction of the maximum is reduced to only 10%-20%. Some of the overprediction may be due to autocorrelations (e.g., dependent sampling) in the actual hourly data. A modified lognormal approach to predicting maxima involves reducing the theoretical yearly sample size; this approach can account for the autocorrelations in a very approximate way.

- The Gamma distribution seriously underpredicts yearly one-hour NO_2 maxima. The lognormal distribution, fit to the upper range of the hourly concentration data, seems preferable to the Gamma distribution for the purposes of characterizing expected yearly maxima.
- There are four potential uses for mathematical distributions in analyzing maximal NO_2 concentrations: to identify outliers for the data quality check, to estimate the random variance in yearly maxima, to adjust yearly maxima for incomplete sampling, and to characterize patterns in yearly maxima using expected (predicted) maxima rather than measured maxima. For the purposes of this study, the lognormal distribution is appropriate for the first three uses. No distribution is appropriate for the fourth use; it is best to characterize spatial and temporal patterns in yearly maxima by using the actually measured maxima.

Characterization of Present NO_2 Air Quality Levels

- There are 123 monitoring sites which provide at least one year of data from 1972 to 1974. Of these, 120 can be classified as urban; the other 3 are rural/power plant sites. Averages for various categories of urban sites (center city vs. suburban, or industrial vs. commercial vs. residential vs. mobile) all show about the same level of annual mean, 90th percentile, and yearly maximum NO_2 concentrations. The 3 rural/power plant sites are atypical because of their low annual means and very high maximum-to-mean ratios.
- Eighteen of the 120 urban monitoring sites exceed the federal standard for annual mean NO_2. Thirteen of these sites are in the Los Angeles basin; the other five locations are Baltimore, Md.; Springfield, Mass.; Chicago, Ill.; Newark, N.J.; and Elizabeth, N.J. Fourteen nationwide sites exhibit 90th percentiles exceeding 10 pphm. Forty-seven of the

120 urban monitoring sites have yearly one-hour maxima which exceed 25 pphm, but only 4 sites experience yearly one-hour maxima that exceed 50 pphm. The sites with the highest yearly maximal and 90th percentile concentrations are generally the same as the sites with the highest annual mean concentrations; the Los Angeles basin is the national hot spot for annual mean, 90th percentile, and one-hour maximal NO_2 concentrations.

- Within the Los Angeles basin, the spatial distribution of NO_2 concentrations generally corresponds well with the distribution of NO_x emissions. In parts of the Los Angeles region, on a scale of about 50 km, there is evidence that both transport and local effects are important for NO_2. NO_2 concentrations do not follow consistent overall patterns in the New York-New Jersey-New England area. On the scale of this multi-state region (approximately 500 km), localized emissions seem to be more important than regional transport for nitrogen dioxide pollution.

Trends in Nitrogen Dioxide Air Quality

- Five-year trends (1969-1974) in NO_2 concentrations show the following: no change for Los Angeles County (a slow-growth part of the Los Angeles basin), about a 30%-50% increase in Orange County (a high-growth part of the Los Angeles basin), about a 10% decrease at other California sites and in New Jersey, and a large increase (about 30%-50%) in Chicago. Ten-year concentration trends (1964-1974) show about a 10% to 20% increase in Los Angeles County, with larger increases (about 40%) at Stockton, Calif. and Chicago, Ill. For most sites, yearly maximal NO_2 concentrations increase less than (or decrease more than) annual mean NO_2 concentrations.
- For the most part, year-to-year trends in NO_2 concentrations at CAMP sites, New Jersey sites, and Los Angeles sites can be explained in terms of source growth and changes in emission factors. Historical NO_2 trends in Los Angeles show an earlier rise, and then an earlier decline, than NO_2 concentrations at CAMP sites; this reflects the new-car

emission control program which started two years earlier in California and included an NO_x emission standard two years earlier in California than nationwide.

Relationship of Yearly One-Hour Maxima and Annual Means

- Eighty-five percent of the 102 urban monitoring sites have maximum/mean NO_2 ratios between 4 and 8. One location exhibits a maximum/mean ratio slightly less than 4. Only six percent of the locations have maximum/mean ratios greater than 10.
- If a one-hour NO_2 standard were set at 25 pphm, and if maximal and mean NO_2 concentrations responded equivalently to emission changes, the one-hour standard (rather than the present annual mean standard) would be the binding constraint at 88% of the urban locations. If a one-hour NO_2 standard were set at 50 pphm, the annual mean standard would be the binding constraint at 94% of the urban locations.
- There are no broad nationwide patterns in the maximum/mean NO_2 ratio. Also, the maximum/mean ratio for urban sites does not depend significantly on the annual mean concentrations. No consistent patterns in the maximum/mean ratio appear on an intraregional scale in Los Angeles or the New York-New Jersey-New England area.
- The maximum/mean ratio shows a strong downward trend in coastal/central Los Angeles County over the past decade. This area has experienced significant hydrocarbon control. The empirical models of Part II indicate that hydrocarbon control preferentially reduces maximum NO_2 concentrations over mean NO_2 concentrations. Changes in the spatial distribution of emissions may also lead to reductions in the maximum/mean ratio. CAMP sites and other sites in California also show a decreasing maximum/mean ratio. The maximum/mean ratio has remained approximately constant at New Jersey locations and in high-growth areas of the Los Angeles basin.

1.2 SUMMARY OF PART II: EMPIRICAL MODELS OF THE NO_2/PRECURSOR RELATIONSHIP

The objective of Part II is to develop, apply, and test empirical models that indicate the dependence of NO_2 on hydrocarbon and NO_x control.

The findings and conclusions of Part II are summarized below; the summary is organized according to the order of the chapters (7 through 14).

Empirical Analysis of the NO_2/Precursor Dependence

- Historically, experimental studies with smog chambers have provided most of our understanding of the NO_2/precursor dependence. The various smog-chamber studies agree concerning the proportional dependence of NO_2 (average or peak concentrations) on NO_x. Although the individual chamber studies disagree concerning the effect of hydrocarbons on NO_2, a consensus would be that hydrocarbon control yields slight to moderate benefits in terms of maximal NO_2 and produces essentially no effect on annual mean NO_2. Because of disagreements among the chamber studies and because of uncertainties in extrapolating experimental simulations to the atmosphere, there is a need for empirical models that extract information on the NO_2/precursor dependence from ambient monitoring data.
- This report develops empirical control models by combining statistical (regression) equations with simple physical assumptions. The empirical modeling analysis is disaggregated by time of day and by season. The statistical equations for daytime NO_2 use early-morning (6-9 A.M.) hydrocarbons and NO_x as precursor variables. Evening NO_x and late-afternoon oxidant are considered as precursors of nighttime NO_2. The final control models for annual mean NO_2 and yearly maximum NO_2 are based on a synthesis of submodels for each time of day and each season, with linkages between the daytime and nighttime models to account for carryover NO_2 from one part of the day to another.
- The simplified empirical approach followed here is subject to several limitations: the omission of meteorological variables, the neglect of transport phenomena, and the assumption that precursor changes produced by variance in meteorology can be used to model the effect of control strategies. These limitations indicate a need to compare the empirical models against smog-chamber results and historical air quality trends.

Preparation of Data Base for Empirical Modeling

- The empirical models are applied to 8 locations: 2 CAMP sites (Denver and Chicago), 2 Houston sites (Mae and Aldine), and 4 Los Angeles sites (Downtown Los Angeles, Lennox, Azusa, and Pomona). The historical monitoring data for each site are processed, reformulated, checked, and edited before statistical models are attempted.

Seasonal and Diurnal Patterns for NO_2 and its Precursors

- Concentrations of the photochemical precursors (NMHC and NO_x) tend to be greatest during the winter. Oxidant concentrations, however, are greatest during the summer because of increased solar radiation and temperature. Seasonal patterns for NO_2 vary from location to location and apparently reflect competition between higher primary contaminant concentrations in the winter and greater photochemical activity in the summer.
- Diurnal patterns for primary contaminants exhibit two peaks--one in the morning at about 8:00 A.M. and the other in the evening, anywhere from 6:00 P.M. to midnight, depending on the site. Oxidant concentrations exhibit a single maximum, usually between 1:00 P.M. and 5:00 P.M. At most locations, NO_2 concentrations show two maxima--one at about 9:00 A.M. to 10:00 A.M., the other anywhere from 6:00 P.M. to midnight. Although the diurnal patterns for NMHC, NO_x, and NO_2 do exhibit two maxima during the day, the concentrations at other times of the day and night are by no means negligible compared with the peaks.
- For the purposes of the empirical modeling study, the seasonal patterns indicate that a two-season division, winter (October-March) and summer (April-September), is appropriate. The diurnal pollutant patterns lead us to define "daytime" and "nighttime" modeling periods as 6:00 A.M. to 4:00 P.M. and 4:00 P.M. to 6:00 A.M. of the following day, respectively.

Empirical Models Applied to Downtown Los Angeles

- A wide variety of statistical techniques are used to explore the data base for Downtown Los Angeles. These techniques all yield the same qualitative conclusions concerning the dependence of NO_2 on precursors. The most important contributors to daytime NO_2 (both peak and average) are nighttime carryover NO_2 (NO_2 at 6:00 A.M.) and initial NO (NO_x from 6:00 A.M. to 9:00 A.M. minus NO_2 at 6:00 A.M.). Hydrocarbon reductions yield a small, but statistically significant, benefit in terms of daytime NO_2. The hydrocarbon effect is greater for peak NO_2 than average NO_2, is greater in winter than summer, and is greater at high NO_x levels than low NO_x levels.

- Three factors are found to be contributors to nighttime NO_2--carryover NO_2 from the afternoon, early-evening NO, and afternoon oxidant (which presumably combines with evening NO). Hydrocarbon control should decrease afternoon oxidant (assumed proportional to the $NMHC/NO_x$ ratio). This effect is counterbalanced because hydrocarbon control apparently increases carryover NO_2 from the afternoon.
- Statistical analyses involving meteorological parameters indicate that the observed hydrocarbon effect may be partially an artifact produced by unaccounted for weather variables. This finding reinforces the need to check the empirical control models against smog-chamber results and historical trends.

Empirical Models Applied to Various Cities

- The formulation of empirical models for the 8 selected locations proceeds smoothly with the exception of nighttime models for the 2 Houston locations. Complete empirical control models for annual mean NO_2 and yearly one-hour maximum NO_2 are developed for the 6 non-Houston sites.
- The empirical models for all 6 locations (as well as the daytime models for the 2 Houston sites) indicate that, with other factors held constant, both annual mean NO_2 and yearly maximum NO_2 are essentially proportional to NO_x input. The slight deviations away from proportionality that sometimes occur in the empirical models are all in the direction of a less-than-proportional relationship.

- The empirical models for various cities show that hydrocarbon control yields slight, essentially negligible, effects on annual mean NO_2. The models predict that 50% hydrocarbon control decreases annual mean NO_2 by 6% at Downtown Los Angeles, 2% at Lennox, 2% at Azusa, 11% at Pomona, and 0% at Chicago, and increases annual mean NO_2 by 5% at Denver.
- The empirical models indicate that hydrocarbon reductions yield slight-to-moderate benefits for yearly maximum NO_2. Fifty-percent hydrocarbon control reduces yearly maximum NO_2 by 25% at Downtown Los Angeles, 10% at Lennox, 6% at Azusa, 19% at Pomona, 0% at Chicago, and 8% at Denver. Yearly maximum NO_2 occurs under winter/daytime conditions at Downtown Los Angeles, Lennox, Denver, and Houston/Mae; under summer/daytime conditions at Chicago; and under winter/nighttime conditions at Azusa, Pomona, and Houston/Aldine (the 3 downwind receptor sites studied).

Validation of Empirical Models Against Historical Air Quality Trends

- Validation studies for the empirical NO_2 control models are conducted at 10 monitoring sites: 3 in the central Los Angeles area, 3 in the coastal Los Angeles area, 2 in the inland Los Angeles area, 1 in Denver, and 1 in Chicago. Verification of the models against trends at individual monitoring sites attains a mixed level of success, with best results obtained in the central and coastal Los Angeles area. The less successful tests at Azusa and Pomona may indicate that omitting transport relationships in the empirical models is inappropriate for these two sites (as it also seemed to be for Houston/Aldine).
- In an aggregate sense, historical air quality trends confirm the general results of the empirical modeling study. Viewed as a whole, the trends are consistent with the conclusions: (1) a proportional relationship exists between NO_2 and NO_x; (2) a slight to moderate hydrocarbon effect exists for yearly maximum NO_2; and (3) a very slight (if any) hydrocarbon effect exists for annual mean NO_2.

Comparison of Empirical Models Against Smog-Chamber Results

- The general conclusions of the empirical modeling study agree quite well with conclusions based on smog-chamber simulations. Agreement exists with respect to the impact of NO_x and/or hydrocarbon control on both annual mean and yearly maximum NO_2 concentrations.
- The variations in the empirical models from city to city can be due either to errors in the individual models or to real variations in the NO_2/precursor dependence from one location to the next. The differences in the NO_2/precursor relationship found in different smog-chamber studies indicate the latter case is certainly a possibility. However, we are more sure of the general conclusions of the empirical modeling study than we are of the specific models for individual cities.

Conclusions of the Empirical Modeling Study

- The empirical models, in conjunction with smog chamber studies and historical trend analysis, lead us to a basic understanding of the dependence of ambient NO_2 concentrations on precursor control. Although all three approaches involve uncertainties, they all are consistent with the same general conclusions:
  1. With other factors held constant, yearly maximal and annual mean NO_2 concentrations are essentially proportional to NO_x input.
  2. Hydrocarbon control yields slight to moderate benefits in yearly maximal one-hour NO_2; reducing hydrocarbons by 50% should decrease yearly maximal NO_2 by about 10% to 20%.
  3. Hydrocarbon control yields very slight, essentially negligible, benefits in annual mean NO_2.
  4. The exact form of the NO_2/precursor relationship may vary somewhat from one location to the next, depending on climatic conditions, reaction times, and the existing hydrocarbon/NO_x ratio.

PART I:

DESCRIPTIVE ANALYSIS OF THE NATIONWIDE NO_2 DATA BASE

2.0 DATA BASE PREPARATION

The objective of Part I of this report is to characterize nitrogen dioxide air quality in the United States, with particular emphasis on annual mean NO_2 concentrations and maximum one-hour NO_2 concentrations. The data base available for performing this characterization consists of yearly frequency distributions of all hourly NO_2 data in the EPA SAROAD* system. This chapter describes how the available data were processed, checked, and modified for the purposes of the study.

2.1 SAROAD PRINTOUTS OF FREQUENCY DISTRIBUTIONS

The available data for analyzing nationwide NO_2 air quality are printouts of yearly frequency distributions for all hourly NO_2 data in the EPA SAROAD system as of 6 March 1976. Figure 2.1 presents an example of this type of printout. As illustrated in Figure 2.1, the SAROAD printout for each site provides the site code, the name of the monitoring agency, regional population statistics, general information on the site location (address, city, county, state, air basin, and type of surrounding environment), and specific locational parameters (latitude, longitude, UTM coordinates, and elevation). For each year of monitoring activity, the SAROAD printout indicates the 10th, 30th, 50th, 70th, 90th, 95th, and 99th percentile concentrations and the yearly maximum one-hour concentration in units of $\mu g/m^3$. The total number of hourly measurements and the monitoring method are also listed each year. For those years with data for at least 75% of

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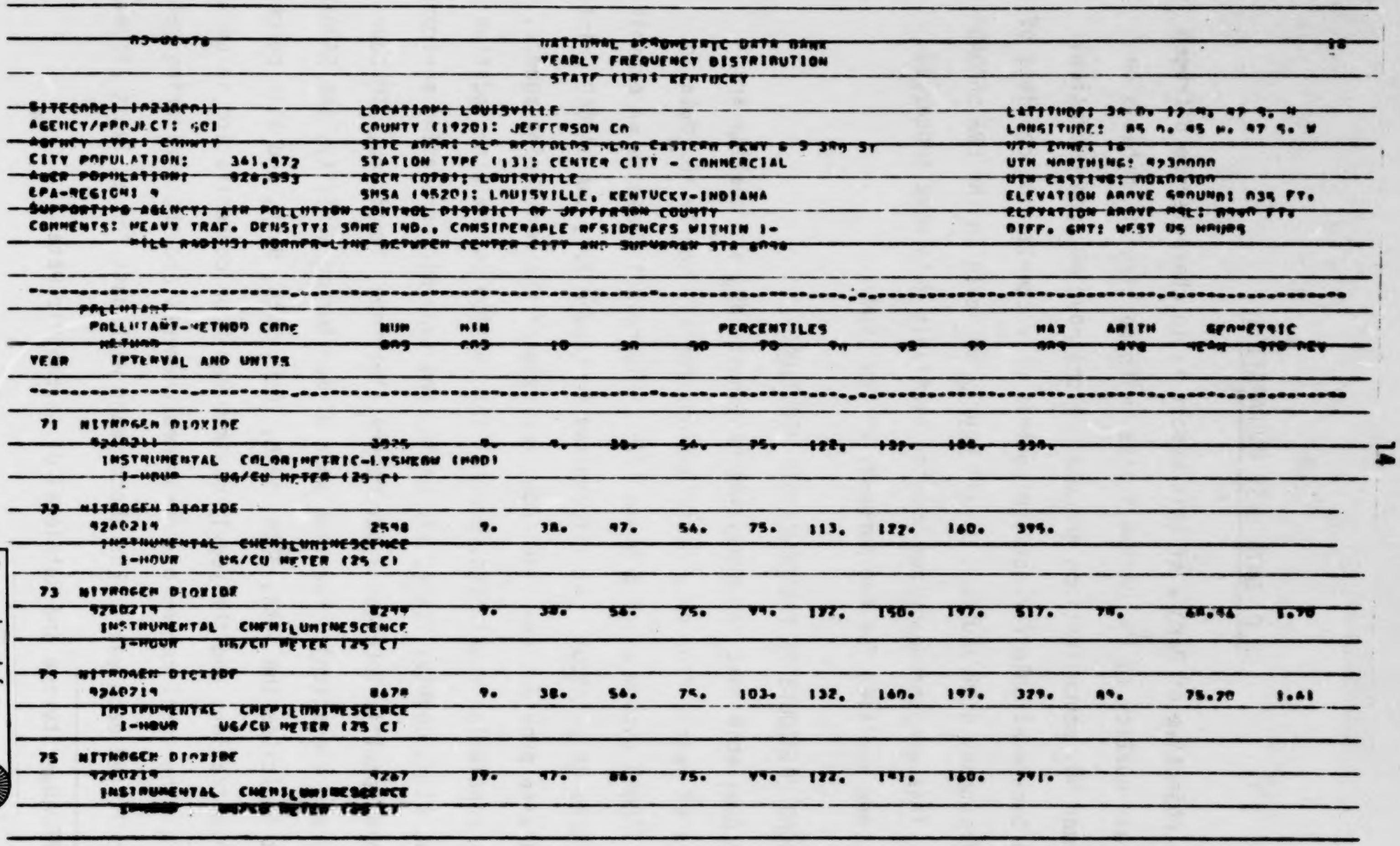
*SAROAD = Storage and Retrieval of Aerometric Data



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       03-08-78                                   NATIONAL AEROMETRIC DATA BANK                                                 18
                                                  YEARLY FREQUENCY DISTRIBUTION
                                                   STATE (18): KENTUCKY

SITECODE: 182380011                LOCATION: LOUISVILLE                                     LATITUDE: 38 D. 12 M. 47 S. N
AGENCY/PROJECT: S01                COUNTY (1920): JEFFERSON CO                              LONGITUDE:  85 D. 45 M. 47 S. W
AGENCY TYPE: COUNTY                SITE ADDR: OLD REYNOLDS BLDG EASTERN PKWY & S 3RD ST     UTM ZONE: 16
CITY POPULATION:     361,472       STATION TYPE (13): CENTER CITY - COMMERCIAL              UTM NORTHING: 4230000
AQCR POPULATION:     926,993       AQCR (078): LOUISVILLE                                   UTM EASTING: [illegible]
EPA-REGION: 4                      SMSA (4520): LOUISVILLE, KENTUCKY-INDIANA                ELEVATION ABOVE GROUND: 035 FT.
SUPPORTING AGENCY: AIR POLLUTION CONTROL DISTRICT OF JEFFERSON COUNTY                       ELEVATION ABOVE MSL: [illegible] FT.
COMMENTS: HEAVY TRAF. DENSITY; SOME IND., CONSIDERABLE RESIDENCES WITHIN 1-                 DIFF. GMT: WEST 05 HOURS
        MILE RADIUS; BORDER-LINE BETWEEN CENTER CITY AND SUBURBAN STA [illegible]

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    POLLUTANT
     POLLUTANT-METHOD CODE          NUM     MIN                       PERCENTILES                          MAX    ARITH     GEOMETRIC
     METHOD                         OBS     OBS     10     30     50     70     90     95     99      OBS    AVG     MEAN   STD DEV
YEAR    INTERVAL AND UNITS
-------------------------------------------------------------------------------------------------------------------------------

 71  NITROGEN DIOXIDE
      4260211                       3925     9.     9.    38.    56.    75.   128.   132.   188.    338.
      INSTRUMENTAL  COLORIMETRIC-LYSHKOW (MOD)
        1-HOUR     UG/CU METER (25 C)

 72  NITROGEN DIOXIDE
      4260214                       2598     9.    38.    47.    56.    75.   113.   122.   160.    395.
      INSTRUMENTAL  CHEMILUMINESCENCE
        1-HOUR     UG/CU METER (25 C)

 73  NITROGEN DIOXIDE
      4260214                       8249     9.    38.    56.    75.    94.   122.   150.   197.    517.    78.      68.46    1.70
      INSTRUMENTAL  CHEMILUMINESCENCE
        1-HOUR     UG/CU METER (25 C)

 74  NITROGEN DIOXIDE
      4260214                       8678     9.    38.    56.    75.   103.   132.   160.   197.    329.    89.      75.20    1.61
      INSTRUMENTAL  CHEMILUMINESCENCE
        1-HOUR     UG/CU METER (25 C)

 75  NITROGEN DIOXIDE
      4260214                       4267    19.    47.    56.    75.    94.   122.   141.   160.    291.
      INSTRUMENTAL  CHEMILUMINESCENCE
        1-HOUR     UG/CU METER (25 C)
```

Figure 2.1 Example of SAROAD Printout of NO_2 Frequency Distributions

Reproduced from best available copy.

all hours, the arithmetic mean, geometric mean, and geometric standard deviation are listed. For the example presented here, Louisville site 011G01, data for 75% of all hours were reported only during 1973 and 1974.*

In this study, data are included only for those stations and years that meet the 75% completeness criterion. The reasons for excluding data which fail the 75% criterion are threefold. First, NO_2 concentrations at many sites follow distinct seasonal patterns. There is a danger that incomplete sampling might be performed only during certain seasons. This could seriously bias the measured frequency distribution. Second, the arithmetic mean, geometric mean, and geometric standard deviation are important for statistical calculations performed in this study. These parameters are not provided for data sets which fail the 75% criterion. The parameters could be estimated from the reported percentile concentrations, but this would introduce another source of error. Third, a quality check is planned for all data to be used in the study. To include the numerous cases which fail the 75% criterion would dilute the project resources available for the quality check. The impact on the quality check program would be especially significant because there appears to be a positive correlation between incomplete data sets and apparently anomalous data sets.

The SAROAD printout of 6 March 1976 included 462 station-years of NO_2 data that met the 75% completeness criterion. In order to facilitate statistical computations, the data for these 462 station-years were punched on computer cards. The information put on each card included the site code, monitoring method, year, number of observations, percentile concentrations, arithmetic mean, geometric mean, and geometric standard deviation. Appendix A presents a printout of these cards (as modified by the data quality analysis discussed later in this chapter).

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*In many cases, the 75% completeness criterion would have been met in 1975 except that some 1975 measurements were not yet reported to SAROAD.

Table 2.1 lists the number of sites, by year, that meet the 75% completeness criteria. It is obvious that the number of sites reporting 75% complete data to SAROAD has increased substantially over the past twelve years. The increase in the number of sites with "complete" data is greatest for the period of 1971 to 1974, with a particularly large jump occurring from 1973 to 1974. The growth in the number of monitoring sites is especially significant outside California; the number of non-California monitoring sites multipled by nearly a factor of seven from 1971 to 1974.

Table 2.1 also lists the average percentage of data for the sites which meet the 75% completeness criterion. The average percentage of data reported by these sites has undergone a steady increase over the years. Thus, not only have more sites attained the 75% criterion in the past few years, but these sites have attained better completeness ratios. The sites in California tend to show higher completeness ratios than sites outside California. This is one indication of the higher quality of the California data base.

Table 2.2 lists the number of sites by year and by monitoring method. There are four monitoring methods: colorimetric-Lyshkow (mod.), chemiluminescence, colorimetric-Griess-Saltzman, and coulometric. Although none of these methods has yet been approved by EPA as a reference method, none of

Table 2.1 Sites Reporting at Least 75% Complete Data for Hourly NO_2 Measurements

Year	NATIONWIDE SITES		CALIFORNIA SITES		NON-CALIFORNIA SITES	
	Total Number of Sites with "Complete" (75%) Data	Average Percentage Data for these Sites	Number of Sites	Average Percentage Data	Number of Sites	Average Percentage Data
1962	4*	80.4%	0*	----	4	80.4%
1963	18	81.0	13	81.2%	5	80.5
1964	18	81.4	14	81.2	4	82.0
1965	19	83.7	13	83.3	6	84.4
1966	22	84.5	17	84.9	5	83.1
1967	32	85.1	23	85.2	9	84.8
1968	26	86.5	20	87.2	6	84.0
1969	29	87.6	23	88.2	6	85.4
1970	29	87.7	21	88.5	8	85.7
1971	33	87.7	25	88.0	8	87.1
1972	52	88.7	39	89.1	13	87.2
1973	58	88.8	37	90.0	31	87.4
1974	112	88.3	57	90.6	55	85.8
Total Number Station-Years	462		302		160	

*There are several monitoring sites in California which meet the 75% completeness criteria for 1962 and prior years. However, California has reported data to SAROAD only for years starting in 1963.

them has yet been designated "unacceptable." Table 2.2 reveals that the colorimetric-Lyshkow (mod.) method accounts for nearly all the California measurements and over 75% of the nationwide measurements. The colorimetric-Griess-Saltzman method accounts for much of the remaining data; this is the method used in the past in the EPA CAMP program.

2.2 DATA QUALITY ANALYSIS

A cursory examination of the original SAROAD printouts indicated likely errors in the data, especially in the maximum one-hour concentrations. For example, the reported frequency distribution for one station was as follows:

Percentile - - - - - -	10%	30%	50%	70%	90%	95%	99%	Maximum one-hour
Concentration (ppm)- -	.005	.02	.03	.04	.05	.07	.11	5.05 (!)

Although the anomalies in the reported data were not always as blatant as the example above, there seemed reason to question the validity of at least 70 of the 462 station-years of data. The maximum one-hour concentration was the only suspicious value in nearly all of these questionable cases. In a very small number of cases, the percentile concentrations (10% to 99%), as well as the maximum one-hour, appeared dubious.

A data quality check was performed to correct and upgrade the data base. The quality check was guided, in part, by the use of a statistical technique which predicted maximum one-hour concentrations for each station-year based on the arithmetic mean and 99th percentile concentrations for that station-year. This technique, which we call the "modified lognormal" approach, is described at length in the next chapter. Its use in the data quality check was to identify outliers by comparing the reported one-hour maxima with the predicted maxima.

Figure 2.2 demonstrates how this was done. Figure 2.2 compares the predicted distribution of "lognormal z values" for yearly one-hour maxima to the histogram of actual z values for the 462 reported one-hour maxima. The data sets corresponding to the right-hand tail of the histogram were considered questionable. All reported maxima which yielded z values greater than 4.3 were subjected to data verification procedures.

The statistical technique identified 60 potential outliers which were submitted to data verification procedures. Several station-years of data, other than those flagged by the statistical technique, were also selected for the verification process. Some of these other data sets were the ones identified as potential problems by staff members of EPA's Office of Air Quality Planning and Standards [1,2]. Other data sets were chosen for verification based on a visual scan of the data base in search of anomalies. Since all of the CAMP data were available to us on magnetic tape, every year of CAMP data was subjected to verification procedures.

The procedures for checking the data were as follows: For each year of CAMP data, all hourly measurements of NO_2, NO, and OX were printed out for the day of maximal one-hour NO_2 concentration. The hour-by-hour pattern of NO_2 concentrations was checked for internal consistency and compared with the patterns of NO and OX concentrations. So that one erroneous NO_2 maximum would not be replaced with a second-highest value that was also in error, the second, third, and fourth days of highest NO_2 concentration were checked by similar procedures. For data other than from CAMP sites, the state or local monitoring agency was contacted, and the reported one-hour maximum was checked against the local data logs. The records of the monitoring agency

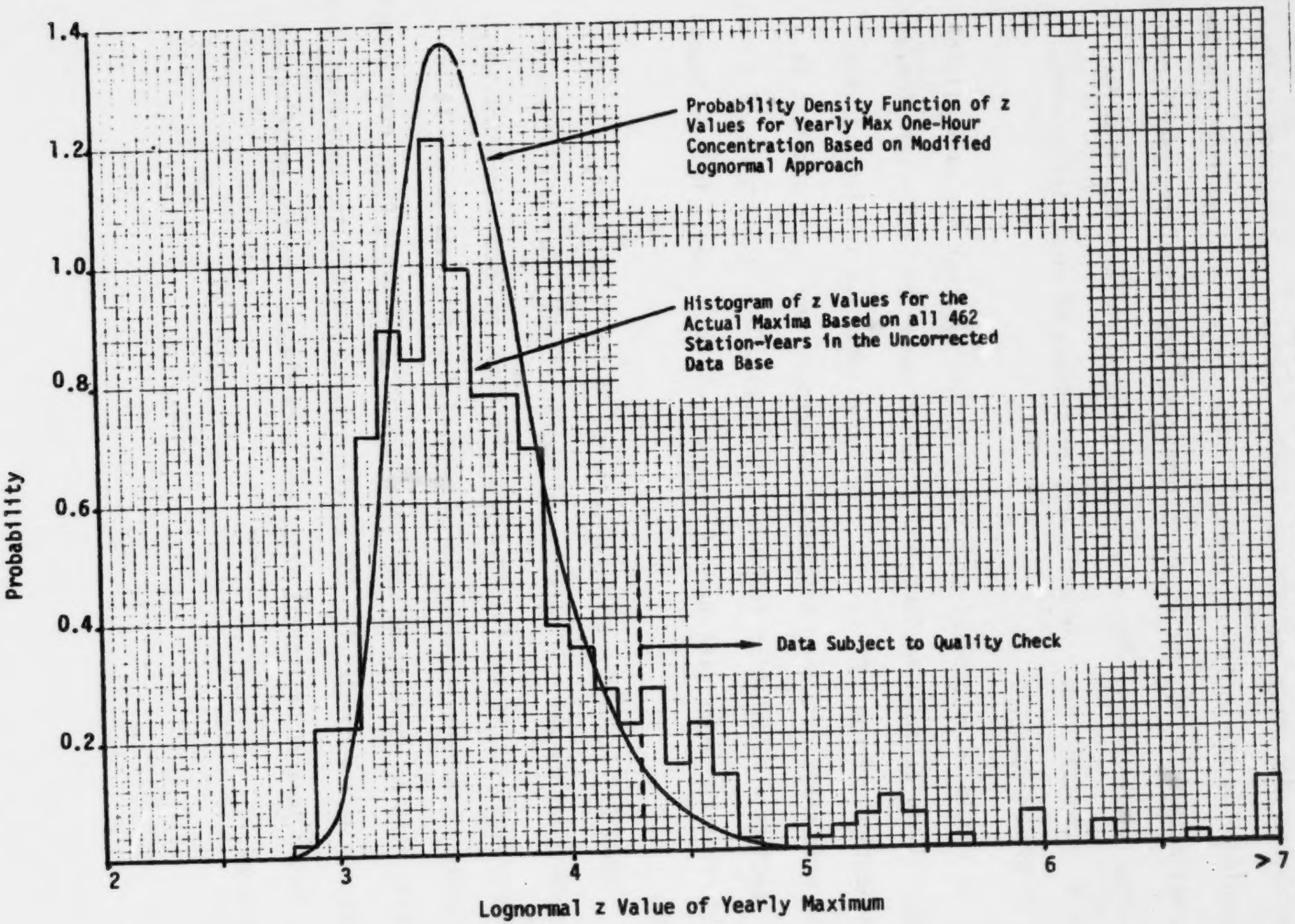

Figure 2.2 Statistical Technique for Identifying Outliers in Reported Maxima

did not agree with the SAROAD output in several instances, implying a transcription error between the local agency and SAROAD. If the records of the local agency did agree with SAROAD, further checks were conducted at the convenience of the monitoring agency. These checks involved examining the diurnal pattern of NO_2 and other pollutants on the day of the yearly maximum one-hour concentration. An especially intensive check of NO_2 data for 1974 in "up-state" New York was conducted because of anomalies pointed out by EPA personnel[2].

It should be emphasized that the data quality check was basically directed toward eliminating large errors which appear as outliers in frequency distributions of the hourly data. The techniques used to flag outliers would miss small errors or moderate-size errors involving a constant factor (such as a calibration factor). Identifying the latter types of errors would require a major data quality program and, even then, might be impossible.

Table 2.3 lists the errors discovered in the data quality check. Forty-two station-years of data needed modifications. Thirty of these involved corrections to the reported yearly maximum one-hour concentration; the other 12 station-years had to be deleted from the data base. It is striking that no corrections were necessary for California data, even though California data accounted for 65% of the station-years in the data base, and even though several California data sets were flagged for the verification procedures.

Table 2.3 Results of Data Quality Check

SITE (SAROAD CODE)	YEAR	MONITORING METHOD	CORRECTIVE ACTION TAKEN	REMARKS
Phoenix, Arizona (030600002-G01)	1967	Colorimetric-Lyshkow (Mod)	Delete data for this year	Conversation with Maricopa County Health Department revealed anamolous data for 1967 and 1968. There may have been calibration and other procedural difficulties during these first two years of instrument operation.
	1968	"	Delete data for this year.	" " " " "
	1973	"	SAROAD reports 1.00 ppm as yearly max one hour. Correct value is .22 ppm.	Transcription error between Maricopa County records and SAROAD system.
New Britain, Connecticut (070680002-F01)	1973	"	SAROAD reports .22 ppm as yearly max one hour. Correct value is .104 ppm.	Transcription errors between Conn. Dept. of Environmental Protection records and SAROAD system.
	1974	"	SAROAD reports 1.40 ppm as yearly max one hour. Correct value is .090 ppm.	" " " " "
Washington, D.C. (090020002-A10)	1965	Colorimetric-Greiss-Saltzman	SAROAD reports .42 ppm as yearly max one hour. Correct value is .23 ppm.	Examination of hourly CAMP data reveals that the highest hour recorded in 1965 is probably invalid. The value used here is the second highest recorded hour in 1965.
Washington, D.C. (090020003-A05)	1974	Chemiluminescence	SAROAD reports .42 ppm as yearly max one hour. Correct value is .17 ppm	Correction recommended by Robert Faoro of EPA-OAQPS.
Chicago, Illinois (141220002-A10)	1964	Colorimetric-Greiss-Saltzman	SAROAD reports .47 ppm as yearly max one hour. Correct value is .33 ppm.	Examination of hourly CAMP data reveals that the recorded .47 ppm is obviously in error (possibly in a decimal point). The .33 ppm value is the second highest reported value for 1964.
	1971	" " "	Delete data for this year.	Examination of hourly CAMP data reveals long strings of high NO_2 values in July 1971. These data are probably all in error. The July values affect the 99% as well as the yearly max and thus the year is not salvageable.
	1973	" " "	SAROAD reports .45 ppm as yearly max one hour. Correct value is .36 ppm.	Examination of hourly CAMP data indicates that the .45 ppm value is dubious. The second highest hour in 1973 is .36 ppm.
Kansas City, Kansas (171800001-H01)	1973	Coulometric	Delete data for this station.	SAROAD values disagree with records of the Kansas City Air Quality Division for both the yearly max and 99th percentile. The Kansas City Air Quality Dviision is unable to supply a correct value for the 99th percentile.
	1974	" "	" " "	" " " " "
Louisville, Kentucky (182380017-A05)	1974	Chemiluminescence	SAROAD reports .39 ppm as yearly max one hour. Correct value is .17 ppm.	Correction recommended by Robert Faoro of EPA-OAQPS
Minneapolis, Minnesota (242260022-H01)	1972	Coulometric	Delete data for this station.	City of Minneapolis Air Pollution Control Division does not consider the data to be reliable. The reported yearly maximum followed a period of instrument failure.
Bellefontaine, Missouri (260200002-G01)	1974	Colorimetric-Lyshkow (Mod)	SAROAD reports .382 ppm as yearly max one hour. Correct value is .236 ppm.	Correction recommended by Robert Faoro of EPA-OAQPS.

Table 2.3 Results of Data Quality Check (Cont'd)

SITE (SAROAD CODE)	YEAR	MONITORING METHOD	CORRECTIVE ACTION TAKEN	REMARKS
St. Louis, Missouri (264280007-H01)	1973	Colorimetric-Lyshkow (Mod)	Delete this station from the data base.	The max one hour value appears too high compared to the rest of the frequency distribution and to max values for other years. The St. Louis City Division of Air Pollution Control can provide no help in determining the real max value.
St. Louis, Missouri (264280061-H01)	1973	" " "	" " "	The max one hour value and other aspects of the reported frequency distribution do not make sense for this year.
St. Louis, Missouri (204280062-H01)	1973	" " "	" " "	" " " "
St. Louis, Missouri (264280063-H01)	1973	" " "	" " "	" " " "
Rosebud, Montana (271360028-F03)	1974	Colorimetric-Lyshkow (Mod)	" " "	All reported values for this station are below the minimum detectable (.005 ppm). The Montana Air Quality Bureau indicates that the ambient NO_2 levels are actually that low. The data are deleted since there is no information for ascertaining the frequency distribution of various concentrations.
Reno, Nevada (290480005-I01)	1973	Coulometric	SAROAD reports 1.11 ppm as yearly max one hour. Correct value is .182 ppm.	Transcription error between Washoe County records and SAROAD system.
	1974	" " "	SAROAD reports 4.56 ppm as yearly max one hour. Correct value is .335 ppm.	" " " "
Phillipsburg, New Jersey (314240002-F01)	1972	Colorimetric-Griess-Saltzman	SAROAD reports .39 ppm as yearly max one hour. Correct value is .17 ppm.	Examination of hourly values reveals that the reported maximum is very dubious. It is replaced with the second highest value for the year.
	1973	" " "	SAROAD reports .328 ppm as yearly max one hour. Correct value is .19 ppm.	" " " "
Buffalo, New York (330660005-F01)	1974	Colorimetric-Lyshkow (Mod)	SAROAD reports .38 ppm as yearly max one hour. Correct value is .17 ppm.	Scan of hourly data reveals that the reported maximum is very dubious. It is replaced by the second highest value for the year.
Buffalo, New York (330660007-F01)	1974	" " "	SAROAD reports .59 ppm as yearly max one hour. Correct value is .13 ppm. Also correct 99th percentile from .107 ppm to .097 ppm.	Scan of hourly data reveals that the reported maximum and several other high values are very dubious.
Kingston, New York (333500002F01)	1974	" " "	SAROAD reports .25 ppm as yearly max one hour. Correct value is .09 ppm.	Scan of hourly data reveals that the reported maximum and several other high values on the same day are very dubious
Niagra Falls, New York (334740006-F01)	1974	" " "	SAROAD reports .31 ppm as yearly max one hour. Correct value is .17 ppm. Also correct 99th percentile from .107 ppm to .097 ppm.	Scan of hourly data reveals that the reported maximum and several other high values are very dubious.
Rochester, New York (335760004-F01)	1974	" " "	SAROAD reports .33 ppm as yearly max one hour. Correct value is .11 ppm.	Scan of hourly data reveals that the reported maximum and two other high values are very dubious.

Table 2.3 Results of Data Quality Check (Cont'd)

SITE (SAROAD CODE)	YEAR	MONITORING METHOD	CORRECTIVE ACTION TAKEN	REMARKS
Schenectady, New York (336020003-F01)	1974	Colorimetric-Lyshkow (Mod)	SAROAD reports .20 ppm as yearly max one hour. Correct value is .09 ppm.	Scan of hourly data reveals that the reported maximum is very dubious. It is replaced by the second highest value for the year.
Syracuse, New York (336620011-F01)	1974	" " "	SAROAD reports 1.70 ppm as yearly max one hour. Correct value is .13 ppm.	The value of 1.70 ppm is a transcription error between New York State Department of Environmental Conservation and the SAROAD system. The second highest value, .23 ppm, was also invalidated by a scan of the hourly NO_2 data.
Utica, New York (336880004-F01)	1974	" " "	SAROAD reports .24 ppm as yearly max one hour. Correct value is .13 ppm.	Scan of hourly data reveals that the reported maximum and several other high values on the same day are very dubious.
Cincinnati, Ohio (361220003-A10)	1964	Colorimetric-Griess-Saltzman	SAROAD reports .34 ppm as yearly max one hour. Correct value is .24 ppm.	Examination of hourly CAMP data reveals that .34 ppm value is obviously in error. The .24 ppm value is the second highest for the year.
Lancaster City, Pennsylvania (394660007-F01)	1974	Chemiluminescence	SAROAD reports .272 ppm as yearly max one hour. Correct value is .084 ppm.	The reported .272 ppm value has been invalidated by the Pennsylvania Department of Environmental Resources.
Philadelphia, Pennsylvania (397140002-A05)	1973	" " "	SAROAD reports .65 ppm as yearly max one hour. Correct value is .29 ppm.	Correction recommended by Jerry Ackland of EPA-NERC/RTP.
Philadelphia, Pennsylvania (397140004-H01)	1972	Colorimetric-Lyshkow (Mod)	SAROAD reports 5.05 ppm as yearly max one hour. Correct value is .25 ppm.	Transcription error between Philadelphia Air Management Services and SAROAD system.
Providence, Rhode Island (410300005-F01)	1972	Colorimetric-Griess-Saltzman	SAROAD reports .45 ppm as yearly max one hour. Correct value is .26 ppm.	Transcription error between Rhode Island Department of Health and SAROAD system.
	1973	" " "	SAROAD reports .531 ppm as yearly max one hour. Correct value is .175 ppm.	" " " "
Providence, Rhode Island (410300007-F01)	1972	" " "	SAROAD reports .35 ppm as yearly max one hour. Correct value is .16 ppm.	" " " "
	1973	" " "	SAROAD reports .39 ppm as yearly max one hour. Correct value is .13 ppm.	" " " "
	1974	" " "	SAROAD reports .465 ppm as yearly max one hour. Correct value is .205 ppm.	" " " "
Nashville, Tennessee (442540010-G01)	1974	Colorimetric-Lyshkow (Mod)	Delete this station from the data base.	Metropolitan Nashville/Davidson County Health Department indicates that all data from this station have been invalidated.

2.3 REFERENCES

1. R. Faoro, "1974 NO_2 Maximum Values," Memorandum to W.F. Hunt and J. McGinnity, EPA Office of Air Quality Planning and Standards, RTP, North Carolina, 26 January 1976.

2. D. Iverach, EPA Office of Air Quality Planning and Standards, Personal communication concerning NO_2 data quality for stations in New York state, December 1977.

3.0 STATISTICAL DISTRIBUTIONS FOR CHARACTERIZING MAXIMAL CONCENTRATIONS

One of the major objectives of the present study is to characterize yearly maximum one-hour NO_2 concentrations. The simplest and most direct way of performing this characterization is to base it on the actually measured yearly maxima for various stations and various years. An alternative is to base the characterization on expected yearly maxima, with the expected maxima determined by fitting statistical functions to the concentration frequency distribution for each station-year.

The latter approach, involving calculated expected values, offers four basic advantages. First, calculating expected maxima facilitates the data quality check since a comparison of the expected maxima to recorded maxima helps to identify potential outliers in the recorded data. Second, the statistical methods used to compute the expected maxima also provide an estimate of the variance in yearly maximum concentrations at each location. The variance in the yearly maximal concentrations can be estimated from as little as one year of data. Using actually measured maxima to estimate the variance in yearly maxima requires several years of data and is subject to errors caused by the confounding of long-term trends with year-to-year stochastic fluctuations.

A third advantage is that the expected maxima are calculated assuming a full year of sampling, 8760 hours. Unlike the expected maxima, the measured maxima depend on the number of samples taken per year, ranging from around 6600 to 8600 for the data base in question. In this regard, the statistical techniques used to determine the expected maxima offer a side benefit: they provide a method for adjusting the measured maxima in order to account for incomplete (less than 100%) sampling during the year. Such an adjustment will be made to all the measured maxima in this study.

A final advantage is that expected maxima, determined from the entire concentration frequency distribution, are statistically more "robust" than measured yearly maxima; i.e., they are based on a larger number of measurements. The robust nature of the expected maxima may help in the identification of geographic and temporal patterns in NO_2 concentrations. Geographic and temporal patterns are often difficult to discern in measured yearly NO_2 maxima because of the large random variance (standard deviation typically ± 20%) associated with these once-per-year events. Statistical parameters of NO_2 air quality that are associated with a large number of measurements, e.g., annual mean concentrations, show less variance from year to year, typically ± 11%.

The potential advantages of using calculated expected values to characterize yearly maximal NO_2 concentrations justify an attempt to formulate a statistical method of determining expected maxima. This chapter describes the effort made in the present study to develop methods of predicting expected maxima. Section 3.1 deals with a method based on the lognormal distribution, while Section 3.2 describes a method based on the Gamma distribution. Section 3.3 discusses the usefulness of these statistical methods for the purposes of this study. It is concluded that the statistical approach involving expected maxima is very useful for analyzing data quality, estimating the random variance in yearly maxima, and adjusting measured maxima according to yearly sample size. However, the simple approach involving measured maxima (adjusted to a common yearly sample size) is preferred for analyzing geographic and temporal patterns in maximal NO_2 concentrations.

3.1 A METHOD BASED ON THE LOGNORMAL DISTRIBUTION

The mathematical function most often used to analyze air pollutant frequency distributions is the lognormal distribution function popularized by Larsen and his co-workers [1,2,3,4,5,6]. Both theoretical considerations and empirical evidence indicate that the assumption of lognormality is a good approximation for air pollutant concentrations in many situations [7,8,9,10,11,12]. When properly used, the lognormal distribution can be a valuable tool in studying air quality data. However, important questions have been raised concerning the Larsen techniques and the assumption of lognormality [13,14,15,16]. A degree of caution should be observed whenever the lognormal distribution is used to analyze air quality data, especially in the case of a reactive pollutant such as nitrogen dioxide [11].

3.1.1 The Lognormal Distribution Function

The assumption that a pollutant concentration variable, C, follows a lognormal distribution means that the natural logarithm of the concentration, $\ell n C$, follows a normal distribution. If the probability density function for a normal distribution (with mean, μ, and standard deviation, σ) is denoted by $f(y)$,

$$f(y)dy = \frac{e^{-\frac{1}{2}\left(\frac{y-\mu}{\sigma}\right)^2}}{\sigma\sqrt{2\pi}}\, dy \quad , \qquad (1)$$

then the probability density function for a lognormal distribution is

$$\tilde{f}(C)dC = f(\ell n C)d\,\ell n C = \frac{e^{-\frac{1}{2}\left(\frac{\ell n C\ -\ \ell n m_g}{\ell n\, s_g}\right)^2}}{\sigma C\sqrt{2\pi}}\, dC \quad , \qquad (2)$$

where $\mu \equiv \ell n\, m_g \ = \ell n$ (geometric mean)

and $\sigma \equiv \ell n s_g \ = \ell n$ (geometric standard deviation).

The cumulative frequency for the normal distribution is

$$F(y) = \int_{-\infty}^{y} f(x)dx \quad , \qquad (3)$$

and for the lognormal distribution,

$$\tilde{F}(C) = \int_{0}^{C} \tilde{f}(x)dx$$

$$= \int_{-\infty}^{\ell n C} f(x)dx = F(\ell n C) \quad . \qquad (4)$$

Above, the notation for the lognormal distribution is kept closely tied to the notation for the normal distribution because useful mathematical tables are readily available for the latter. In particular, if we introduce the change of variable

$$z = \frac{y - \mu}{\sigma} \equiv \frac{\ell n C - \ell n m_g}{\ell n s_g} \quad , \qquad (5)$$

then the distribution functions depend only on the variable z and not on the parameters m_g and s_g. Tabled cumulative frequencies for the normal distribution (or in this case, the lognormal distribution) are commonly available in terms of the parameter z.

3.1.2 Maximal Values from Sampling Lognormal Distributions

In this study, we are interested in using the lognormal distribution function to predict expected yearly maximal one-hour concentrations of NO_2. Assuming that we know m_g and s_g for the concentration frequency distribution, and assuming that a yearly sample consists of N = 8760 independent measurements, then the distribution of the yearly maxima can be readily calculated (see Appendix B). For large N, the cumulative frequency distribution for the yearly maxima, C_m, is (approximately)

$$M(C_m) = e^{-N[1 - \tilde{F}(C_m)]} = e^{-N[1 - F(\ell n\ C_m)]} \quad , \qquad (6)$$

where F is the cumulative distribution function for the normal distribution. The median value for the yearly maximum is found by setting $M(C_m)$ equal to $\frac{1}{2}$; i.e., the median of the yearly maxima for given m_g and s_g is obtained by simply solving

$$F(\ell n C_m) = 1 - \frac{\ell n 2}{N} = 1 - \frac{0.693}{N} \quad , \qquad (7)$$

using values for F found in common mathematical tables. The z value which is the solution to Equation (7) for N = 8760 is z = 3.78. That is, for samples of size 8760 drawn independently from a lognormal distribution, the median of the maxima of those samples would be determined from

$$3.78 = \frac{\ln C_m - \ln m_g}{\ln s_g}$$

or

$$C_m = m_g \, s_g^{3.78} \quad . \tag{8}$$

The expected value of the maximum for a sample of size 8760 corresponds to a z value of 3.82. Thus, for the expected maximum*

$$C_m = m_g \, s_g^{3.82} \tag{9}$$

3.1.3 Adjusting Measured Maxima for Incomplete Sampling

As an aside, we note that the above results are useful for a special task--adjusting measured maxima to account for incomplete sampling. Since the sample sizes in our data base can range from 6570 to 8760 hours per station-year, the recorded maxima are always less than or equal to the actually occurring maxima during all 8760 hours. The lower the number of sampling hours, the more likely it is that the recorded maximum is less than the actual maximum. The recorded maxima should be adjusted upward to account for incomplete sampling. To make this adjustment, Equation (7) can be solved for the median z value, call it z', for the distribution of maxima corresponding to the actual sample size, N'. The recorded maximum can then be adjusted upward by a factor of

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*The expected maximum is computed by integrating the function $C_m \frac{d\,M(C_m)}{d\,C_m}$. Note that Larsen's approximate formula for the expected maximum is $C_m = m_g \, s_g^{3.81}$.

$$\frac{C_m}{C'_m} = \frac{m_g\, s_g^{3.78}}{m_g\, s_g^{z'}} = s_g^{\,3.78 - z'} \quad . \qquad (10)$$

Table 3.1 provides estimates of z' for various sample sizes.

Table 3.1 Median z Values for the Maximum As a Function of Sample Size

Sample Size, N'	Median z' Value
8760	3.78
8000	3.76
7000	3.72
6000	3.68
5000	3.64
4000	3.58
3000	3.50

All yearly maximal values reported in this and subsequent chapters have been adjusted according to Equation (10). The adjustment factors were not of great consequence; they ranged from around 1.005 to 1.07 for the various station-years. The results of this study should be insensitive to the specific assumptions (e.g., lognormality) which were made in deriving the correction factors for incomplete sampling.

3.1.4 Test of Theory for Predicting Expected Maxima

Equations (6) through (9) provide a means for predicting expected yearly maximal NO_2 concentrations based on the entire frequency distribution of concentrations. Before this method is accepted as valid, it should be verified by comparing the predicted maxima with the actual maxima. Equation (6), which forms the foundation for the method, can be tested simultaneously against all 450 station-years in the data base. This is accomplished by using the z parameter which puts the lognormal distribution in a universal mathematical form, independent of m_g and s_g. Equation (6) will predict the theoretical distribution of the z values for the maxima. This theoretical distribution can be verified by comparison with the distribution of z values for the actual maxima.

The z values for the actual maxima are calculated according to Equation (5),using the (adjusted) recorded maxima, geometric mean, and geometric standard deviation specific to each individual station-year. In testing the methodology, we start by using the geometric mean (m_g) and geometric standard deviation (s_g) for each station-year as listed on the SAROAD output. These listed values for m_g and s_g are the geometric mean and geometric standard deviation calculated from all the measured concentrations each year.

Figure 3.1 compares the theoretical distribution of z values for the maxima (assuming 8760 independent samples per year) with the histogram of z values for the actual maxima. The disagreement is obvious. The histogram for the actual maxima is slightly more spread out than the theoretical distribution, and the median of the histogram ($z = 2.99$) is substantially lower than the median of the theoretical distribution ($z = 3.78$). The predicted maxima based on the lognormal theory would tend to be greater than actually occurring maxima. For typical geometric standard deviations, ranging from 1.5 to 2.5, the lognormal theory would tend to overpredict the maximum by 30% to 100%.

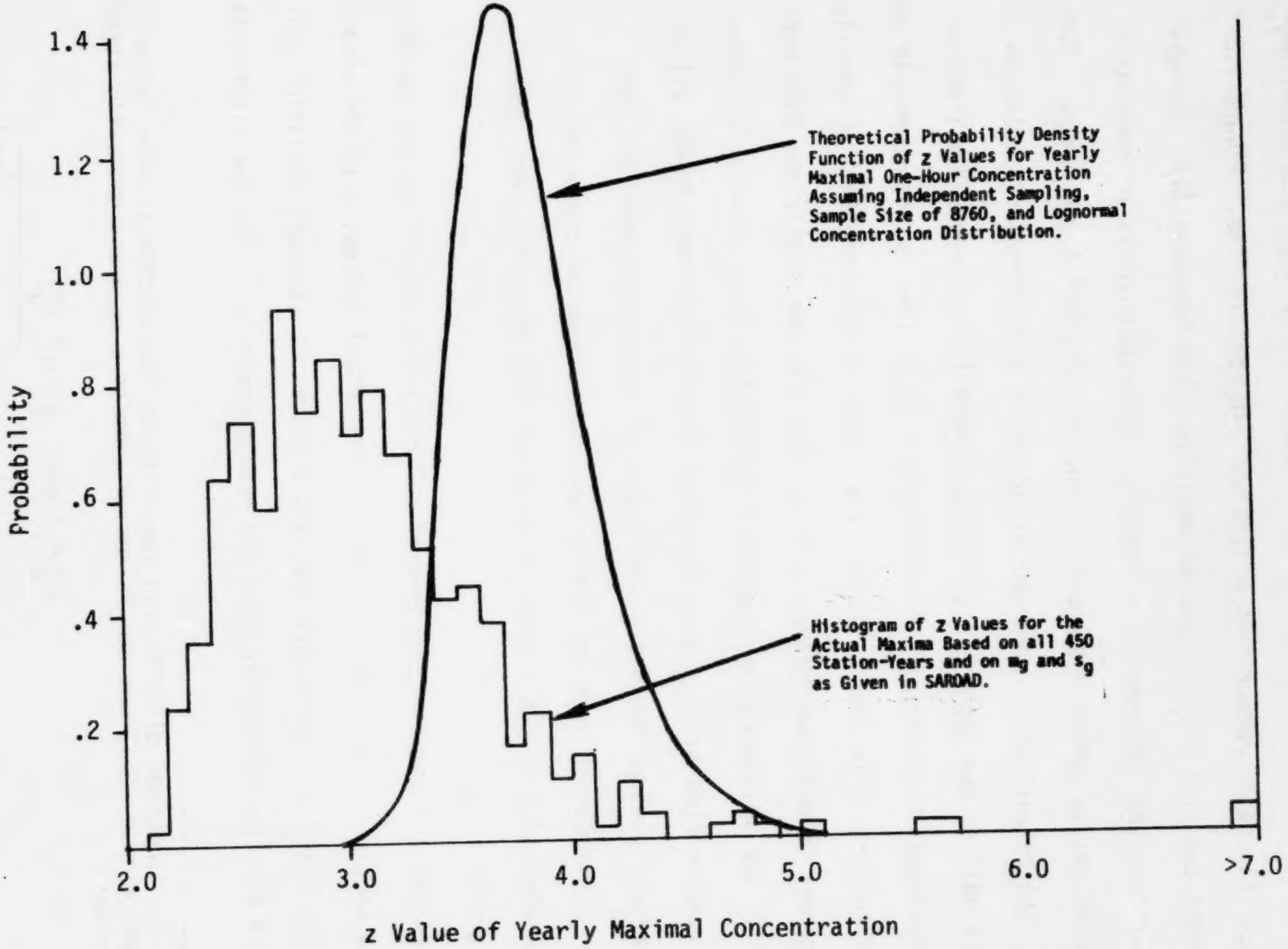

Figure 3.1 Comparison of Theoretical Distribution of Maximal z Values with Actual Data (m_g and s_g as Given in SAROAD)

Much of the disagreement in Figure 3.1 may be due to the assumption that the entire concentration frequency distribution is lognormal. Hourly NO_2 concentrations often follow an "s-shaped" curve when plotted on log-probability paper rather than a straight (lognormal) line. Figure 3.2 presents examples of this type of deviation from lognormality. Because of the "s-shape" phenomenon, a lognormal distribution fit to the entire range of yearly concentrations will tend to overpredict the maxima. This error can be partially corrected for by using a lognormal distribution that is fit only to the upper end of the concentration frequency distribution. For instance, a lognormal distribution can be defined by the geometric mean and 99th percentile concentration, the geometric mean and 95th percentile, the geometric mean and 90th percentile, the 90th percentile and 99th percentile, the arithmetic mean and 99th percentile, etc. Several of these alternate methods of fitting a lognormal distribution were tried; all of the methods yielded about the same level of improvement over the lognormal distribution that was fit to the entire range of concentrations. The method based on the arithmetic mean and 99th percentile was chosen for further study.

Figure 3.3 compares the theoretical distribution of z values for the maxima to the histogram of z values for the actual maxima, with the histogram now based on a geometric mean and a geometric standard deviation calculated from the arithmetic mean and 99th percentile.* The two distributions

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*The lognormal distribution specified by the arithmetic mean (m) and 99th percentile (C_{99}) has the following geometric mean and geometric standard deviation:

$$m_g^* = m \exp[-\frac{1}{2}\ \ell n^2\ s_g^*]$$

$$s_g^* = \exp\left[2.33 - \sqrt{2.33^2 - 2\ \ell n \frac{C_{99}}{m}}\right]$$

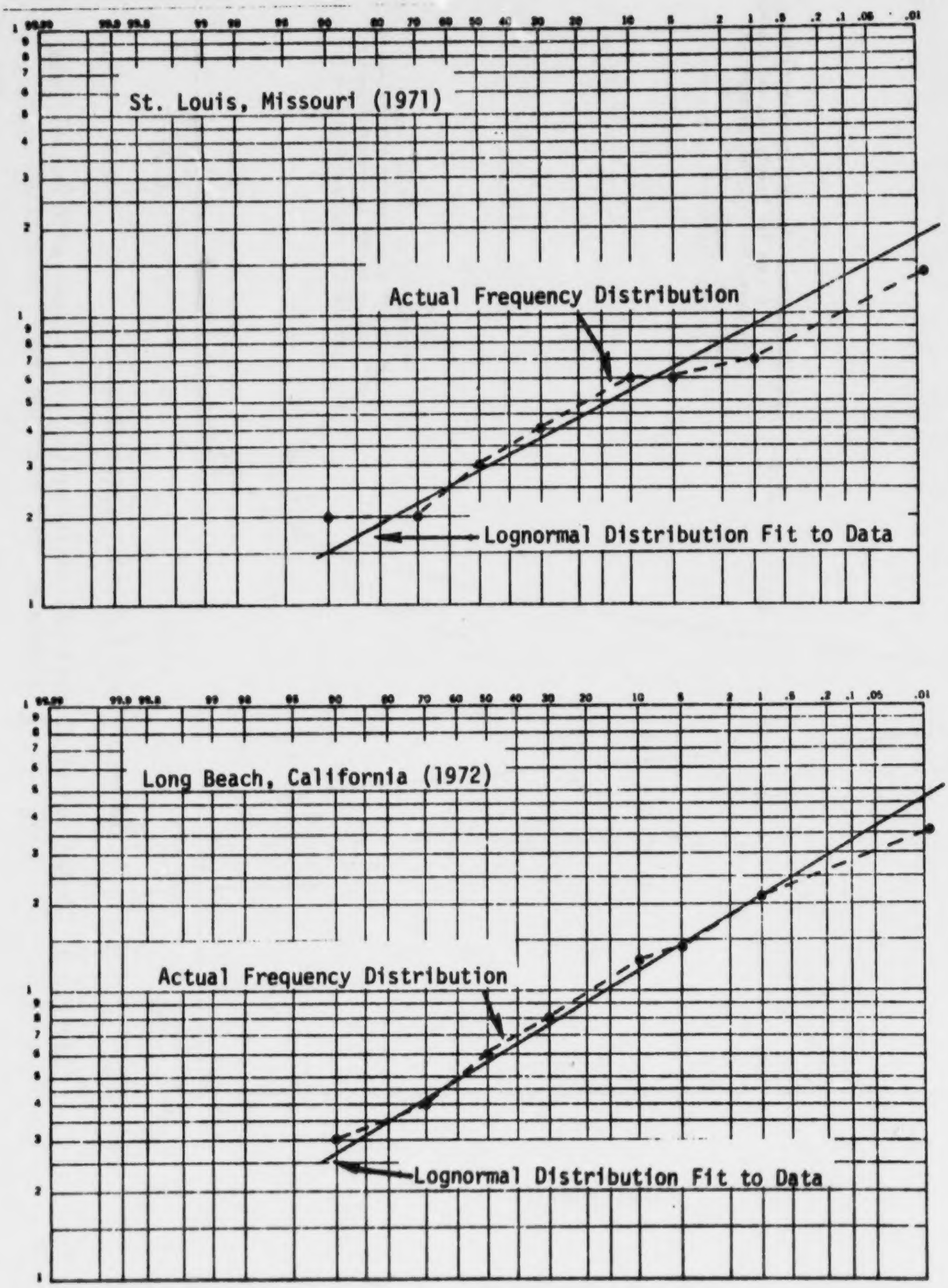
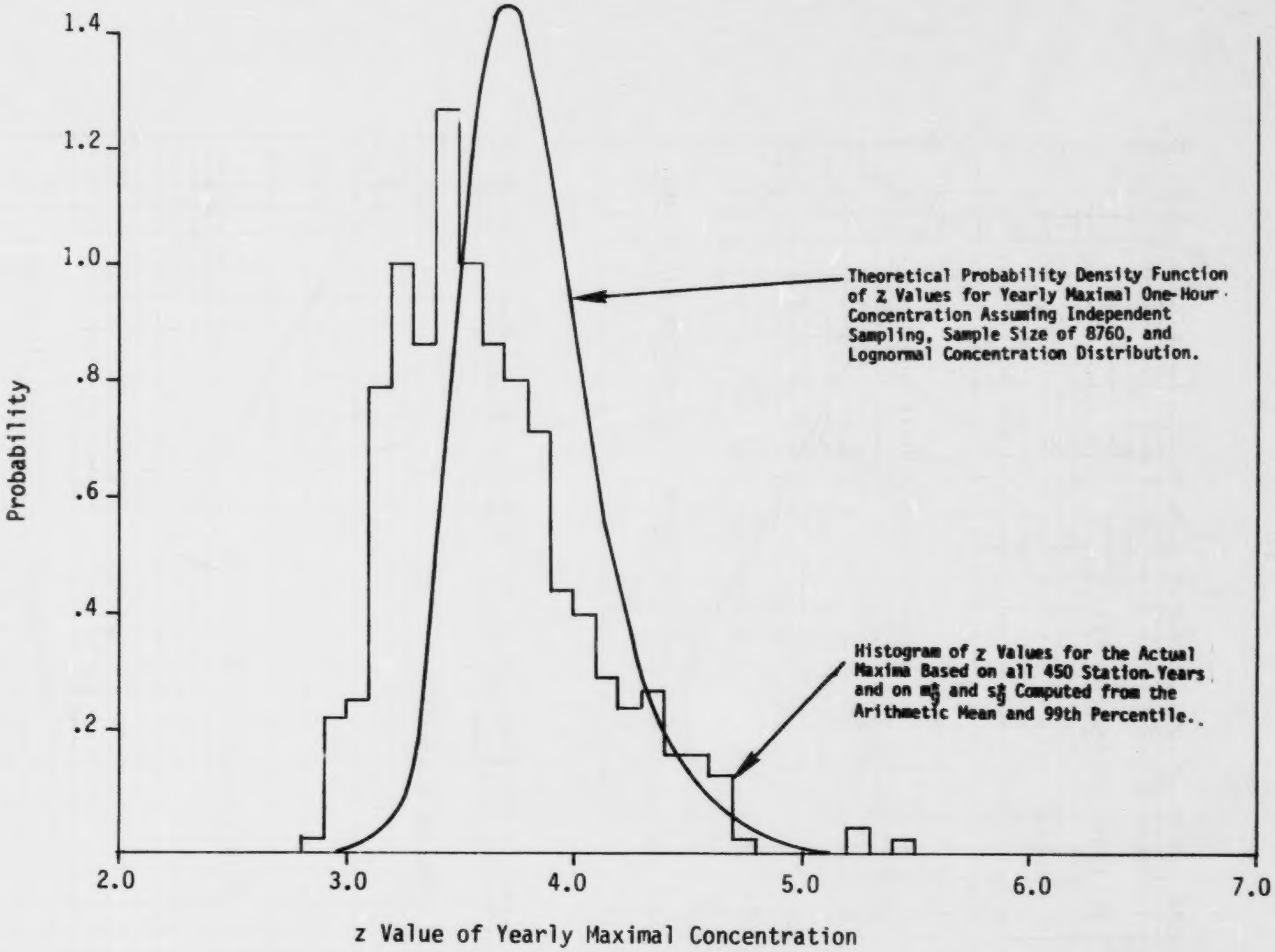


Figure 3.2 Example Frequency Distributions for Hourly NO_2 Concentrations



Theoretical Probability Density Function of z Values for Yearly Maximal One-Hour Concentration Assuming Independent Sampling, Sample Size of 8760, and Lognormal Concentration Distribution.

Histogram of z Values for the Actual Maxima Based on all 450 Station-Years and on m_g^* and s_g^* Computed from the Arithmetic Mean and 99th Percentile.

Figure 3.3 Comparison of Theoretical Distribution of z Values with Actual Data (m_g^* and s_g^* Calculated from Mean and 99th Percentile)

have approximately the same width, and the median of the histogram (3.58) is not far from the median of the theoretical distribution (3.78). Since the theoretical distribution is still centered around a higher z value than is the histogram, predicted maxima based on the lognormal theory would still tend to be greater than actually occurring maxima. The overprediction of the maxima would typically be about 10% to 20%.

3.1.5. A Modified Lognormal Approach

The method for predicting expected maxima that was developed in Section 3.1.2 and tested in Section 3.1.4 is based on the assumption that each of the 8760 hourly measurements in a year is independent, i.e., that no autocorrelations exist among the hourly NO_2 data. This assumption is obviously incorrect because of the persistence of meteorology over a span of a few hours to a few days and because of the consistent diurnal and seasonal patterns in NO_2 concentrations. The autocorrelations in NO_2 concentrations may explain why measured maxima tend to be lower than the maxima predicted by the lognormal theory. Because of the autocorrelation, the number of "independent" conditions that are being sampled are, in effect, less than the assumed value of 8760. This decreases the chance of attaining very high concentrations.

The above observation suggests a way to improve the method of predicting expected NO_2 maxima. It might be possible to discount for autocorrelation in the data by reducing the sample size used to compute the theoretical distribution of yearly maxima. To provide a fit to the nationwide air quality data, the "effective" sample size can be chosen so that the median of the theoretical distribution in Figure 3.3 matches the median of the histogram (which is 3.58). This value for the sample size turns out to be 3990.

The results of this "modified lognormal approach" are presented in Figure 3.4. The median of the theoretical distribution has been force fit to the median based on the nationwide data. It is somewhat encouraging, however, that the shape of the histogram appears to agree fairly well with the shape of the theoretical curve. A Kolmogorov-Smirnov (K-S) test was run to determine if the two distributions are significantly different. The K-S test rejected the hypothesis that the two distributions are the same at a significance level of 5%; i.e., there is less than a 5% chance that the two distributions are identical. Since the sample size is large (450), it is not obvious if a statistically significant difference between the distributions is really of practical importance; i.e., the difference between the distributions may be very small but still statistically significant.

3.1.6 Predicting Expected Maxima

The modified lognormal approach described in the previous section can be used to predict expected maxima for any station-year as follows:

Input Data:

1. Arithmetic mean NO_2 concentration, m
2. 99th percentile NO_2 concentration, C_{99}.

Calculations:

1. Compute m_g^* and s_g^* corresponding to m and C_{99} (see footnote on page 36 for formulas).

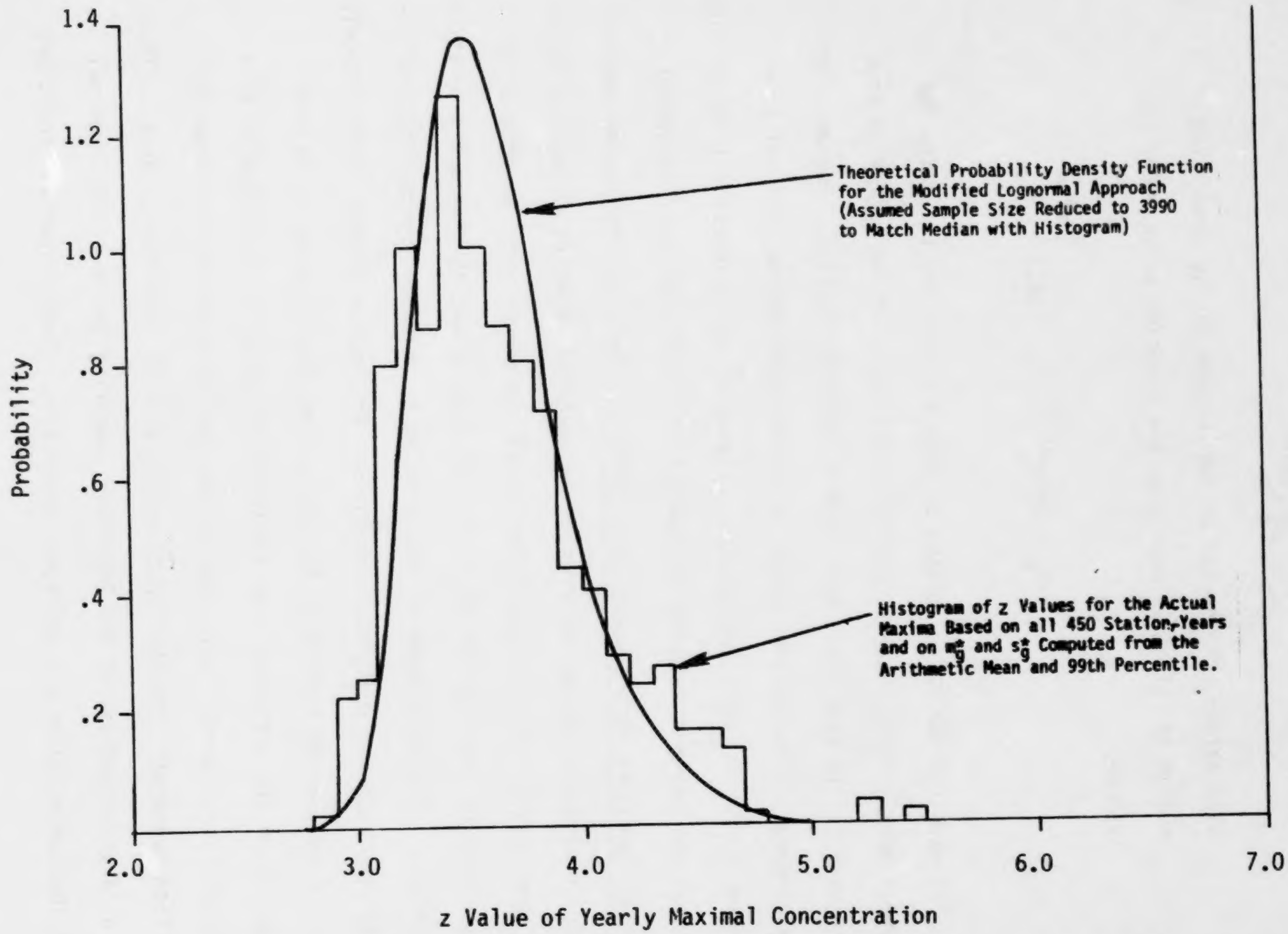


Figure 3.4 Comparison of Theoretical Distribution of z Values with Actual Data (Modified Lognormal Approach)

2. Calculate the expected value of the maximum according to

$$C_m = m_g^* s_g^{*3.62}. \qquad (11)$$

Alternately, the median of the maximum can be used. The median is slightly lower than the expected value. For the median,

$$C_m = m_g^* s_g^{*3.58}. \qquad (12)$$

The expected maxima calculated by this approach may be useful for certain applications, such as providing estimates of the yearly maximum when very little data (less than 3000 measurements) exist. However, for the purposes of the present study, using expected maxima does not seem worthwhile for at least two reasons. First, we are interested in describing spatial and temporal patterns in maximal NO_2 concentrations, including special locations with unusual distributions. The predicted-maxima approach would involve the assumption that NO_2 concentrations at all locations follow the same type of distribution. Forcing all locations into the mold of a single type of distribution would distort some of the special and interesting situations. The importance of this problem is evidenced by testing the lognormal approach for individual locations. Kolmogorov-Smirnov tests indicate that 13 of the 149 individual locations have distributions of maximal z values which are different from the modified lognormal distribution at a 1% significance level. Thirty-one of the 149 locations deviate from the modified lognormal distribution of maxima at a 5% significance level. Thus, for a large percentage of the locations, adopting the modified lognormal distribution would be a significant distortion. These "special" locations occur throughout the country and are characterized by either unusually high or unusually low maximal z values.

The second reason for not using expected maxima in this study is even more fundamental. The one basic advantage that expected maxima might have over actually measured maxima is less variance. The expected maximum is based on two statistics (the annual mean and 99th percentile) that are more robust than the measured yearly maximum. Thus, the expected maximum should fluctuate less from year to year than the measured maximum. This decreased variance should make it easier to discern geographic and temporal patterns in yearly NO_2 maxima. In reality, this advantage is inconsequential. For a given location, the standard deviation of the expected maximum is typically ± 18% from year to year. This is almost as large as the standard deviation of the measured maximum (± 20%). The reason for the large variance in the expected maximum appears to be a compounding of the variance in the annual mean (± 11%) with the variance in the 99th percentile (± 13%). In any case, using expected maxima does not achieve the anticipated decrease in random, year-to-year variance.

3.2 A METHOD BASED ON THE GAMMA DISTRIBUTION

The basic problem in using the (unmodified) lognormal distribution to calculate expected maximal concentrations for nitrogen dioxide is overprediction. The lognormal distribution appears to have a "heavier tail" than actual frequency distributions of NO_2 concentrations. Other mathematical functions, with lighter tails, might provide better predictions of maximal NO_2 concentrations. Light-tail mathematical functions that have been recommended in the literature are the Gamma distribution, the Weibull distribution, and the exponential distribution.

The resources allocated to this study do not permit a thorough investigation of several alternative mathematical distributions as applied to NO_2 data. However, it is worthwhile to test at least one "light-tailed" distribution. The Gamma distribution was selected for this test.

3.2.1. The Gamma Distribution

The probability density function for a pollutant concentration variable following a Gamma distribution is

$$g\ (C) = \frac{C^{\alpha-1}\ e^{-C/\beta}}{\Gamma(\alpha)\ \beta^{\alpha}}\ , \qquad (13)$$

where $\alpha > 0$,

$\beta > 0$,

and $\Gamma(\alpha)$ = Gamma function of α.

The cumulative frequency of the Gamma distribution,

$$G\ (C) = \int_0^C g(x)\ dx, \qquad (14)$$

is listed in mathematical tables. Unlike the normal distribution, which can be put in a universal form by a change of variable to the z parameter, no change of variable exists which makes the Gamma distribution independent of both α and β. A partial normalization is accomplished with

$$t = C/\beta. \qquad (15)$$

Tables for the cumulative frequency distribution are typically found in terms of the variable t. However, a separate table is required for each value of α.

For the purpose of predicting expected yearly maxima, the best results for the lognormal distributions were obtained when the distribution was fit to the "upper end" of the actual concentration data. Specifically, the lognormal distribution was fit to the arithmetic mean (m) and the 99th percentile (C_{99}). To be consistent, the Gamma distributions will also be fit to the arithmetic mean and 99th percentile. This can be done by choosing α according to the following table:

C_{99}/m	α	C_{99}/m	α
2.25	5.5	3.02	2.5
2.32	5.0	3.32	2.0
2.41	4.5	3.78	1.5
2.51	4.0	4.61	1.0
2.64	3.5	6.64	0.5
2.82	3.0	∞	0

and by choosing β as

$$\beta = m/\alpha \quad . \qquad (16)$$

3.2.2 Maximal Values from Sampling Gamma Distributions

Assuming that a yearly sample consists of N = 8760 independent measurements, then the distribution of yearly maxima can be readily calculated (see Appendix B). For large N, the cumulative frequency distribution for the yearly maximum, C_m, is

$$M(C_m) = e^{-N[1 - G(C_m)]} \ , \qquad (17)$$

where G is the cumulative distribution function for the Gamma distribution. This distribution can be shown to be approximately (see Appendix B)

$$M(C_m) = e^{-e^{-s}} \qquad (18)$$

where

$$s = \frac{C_m}{\beta} - \Delta, \qquad (19)$$

and Δ is the solution to

$$\frac{1}{\Gamma(\alpha)} \Delta^{\alpha-1} e^{-\Delta} = \frac{1}{N} \ . \qquad (20)$$

Using Equation (18), the median value of the maximum can be shown to be

$$C_m = \beta[\Delta - \ell n(\ell n 2)]. \quad (21)$$

The expected value of the maximum is

$$C_m = \beta\,(\gamma + \Delta), \quad (22)$$

where γ = Euler's Constant = 0.5772

3.2.3 Test of Theory for Predicting Expected Maxima

Equations (18) through (22) provide a means of predicting expected yearly maximum concentrations by using a Gamma distribution. Equation (18), which is the basis for the method, can be tested simultaneously against all 450 station-years in the data base. Equation (18) predicts the theoretical distribution of the "s parameter." This theoretical distribution can be compared with the distribution of actual "s parameters" for all station-years in the data base. The actual s values are calculated according to Equations (19) and (20), using the actual C_m, N = 8760, and α and β determined from the arithmetic mean and 99th percentile for each station-year.

Figure 3.5 presents the results of testing the Gamma distribution against the actual data. The agreement is very poor compared with the equivalent test for a lognormal distribution (Figure 3.3). The median of the theoretical distribution of s values is well below the median of the histogram of actual s values, implying that the Gamma distribution would underpredict yearly maximum concentrations. Also, the theoretical distribution has much less spread than the histogram. This means that the Gamma

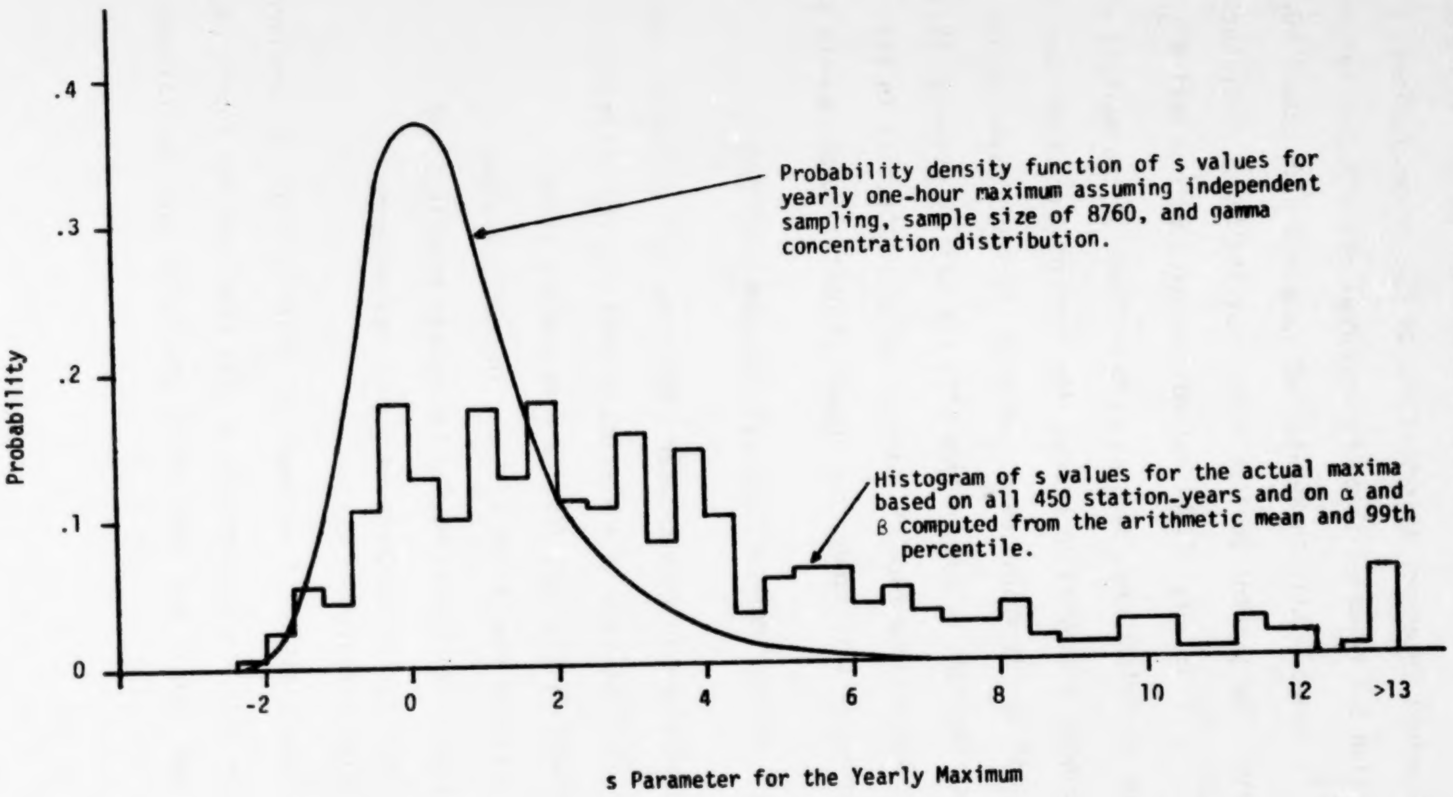


Figure 3.5 Comparison of the Theoretical Distribution of s Values with Actual Data (Gamma Distribution Approach)

distribution also underestimates the variance in the yearly maxima. These observations indicate that the Gamma distribution is too "light-tailed" compared with actual frequency distributions of NO_2 concentrations.

Section 3.1 revealed that the lognormal distribution (with a tail $\sim C^{-1} e^{-\ell n^2 C}$) was slightly "heavy-tailed" compared with actual NO_2 frequency distributions. The present section shows that the Gamma distribution (with a tail $\sim C^{\alpha-1} e^{-C}$) is very "light-tailed" compared with actual NO_2 concentrations. Perhaps other distributions, such as certain forms of the Weibull distribution, may provide a compromise between the lognormal and Gamma and may result in a better fit to the actual data. However, further investigation of mathematical distributions is not in line with the main purposes of this study. Only limited use will be made of mathematical distributions in this report. For the purposes of this study, the lognormal distribution appears sufficient.

3.3 SUMMARY: USES OF MATHEMATICAL DISTRIBUTION FUNCTIONS

The introduction to this chapter identified four potential uses for mathematical distributions in analyzing maximal NO_2 concentrations:

1. To identify outliers for the data quality check;
2. To estimate the random variance in yearly maxima;
3. To adjust yearly maxima for incomplete sampling; and
4. To characterize patterns in yearly maxima, using expected (predicted) maxima.

Based on our investigation of mathematical distributions, we conclude that the first three uses are appropriate in this study but the fourth use is not. A summary of our results and conclusions concerning each use follows.

Data Quality Analysis

The "modified lognormal approach" for predicting expected maxima served as a useful method to identify potential outliers among the recorded maxima (see Chapter 2). Station-years for which the actual maximum deviated a large amount from the expected maximum were subjected to a data verification process. The statistical method of identifying outliers was part of a more comprehensive procedure for noting anomalous data that included a visual scan of all the frequency distributions and a detailed examination of hourly CAMP data.

Variance in Yearly Maxima

The modified lognormal approach can provide an estimate of the random variance in yearly one-hour maxima. Using the theoretical distribution function in Figure 3.4, the cumulative frequency range from 16% to 84% is assumed to represent ± 1 standard deviation. The z values for the cumulative 16th and 94th percentiles are 3.32 and 3.91, respectively. Thus, the standard deviation away from the expected maximum ($z = 3.62$) is

$$C_m = m_g^* \, s_g^{*\,3.62 \, {+\,0.29 \atop -\,0.30}} \quad . \qquad (23)$$

The percentage variance in the expected maximum depends on the geometric standard deviation. Table 3.2 presents results based on Equation (23) for values of s_g^* from 1.3 to 2.3 (nearly all station-years of data have values of s_g^* in the range 1.5 to 2.0).

Table 3.2 Variance in Yearly One-Hour NO_2 Maxima

s_g^*	Standard Deviation of Yearly Maxima
1.3	+ 8% - 8%
1.5	+ 12% - 11%
1.7	+ 17% - 11%
1.9	+ 20% - 18%
2.1	+ 24% - 20%
2.3	+ 27% - 22%

Since the average s_g^* for all stations is 1.8, Table 3.2 indicates that the typical variance should be ± 17 or 18%. It is encouraging that this result agrees with the actual variance in yearly maxima. The actual standard deviation of maxima for individual stations (determined for the years 1970 to 1974) averages around ± 20%.

Adjustment for Incomplete Sampling

The sample sizes in our data base, ranging from around 6600 to 8600 hours per year, are all less than 100% complete (8760 hours per year). Thus, the recorded maxima are less than or equal to the actual maxima during all 8760 hours. As discussed in Section 3.1.3, the lognormal distribution can be used to calculate adjustment factors which account for incomplete sampling. These adjustment factors have been applied to the maximum for each station-year in the data base.

As applied to the present data base, the adjustment factors for incomplete sampling are quite small. This is because all station-years in our data base are at least 75% complete. The results of this study should be insensitive to the specific assumptions used in deriving adjustment factors. However, caution should be observed before applying this method to data which are less than 75% complete. The underlying assumptions will be more important for cases requiring large adjustments to the recorded maxima.

Patterns in Yearly Maxima

One of the basic reasons for our investigation of mathematical distributions was to calculate expected maxima for each station-year. It was hoped that the expected maxima would exhibit less random variance that the actual maxima. Eliminating some of the variance would facilitate identifying spatial and temporal patterns in NO_2 maxima.

As it turned out, the benefit gained in terms of reduced variance was insignificant. The year-to-year fluctuations in the expected maxima (calculated from the mean and 99th percentile using the modified lognormal approach) were nearly as great as the fluctuations in the actual maxima. For this reason, and because of the danger that calculating expected maxima might distort some of the interesting special cases, it was concluded that the best approach for characterizing NO_2 maxima is to use actually measured maxima. The measured maxima will be used in this study.

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4.0 CHARACTERIZATION OF PRESENT NO_2 AIR QUALITY LEVELS

This chapter summarizes present nitrogen dioxide air quality in the United States. The results are based on data for the years 1972, 1973, and 1974. The discussion includes three indices of NO_2 air quality--the annual arithmetic mean, the 90th percentile of hourly concentrations, and the yearly one-hour maximum. Geographical patterns in these indices are illustrated nationwide; intraregional patterns are examined within the Los Angeles area and the New York-New Jersey-New England area. This chapter also investigates the effects of local environment (urban vs. rural, commercial vs. industrial, etc.) on NO_2 concentration distributions.

4.1 DATA BASE FOR DESCRIBING PRESENT NO_2 AIR QUALITY

From the overall data base of 450 station-years, data for the years 1972, 1973, and 1974 are chosen for the purpose of describing present air quality levels. Each station with at least one year of complete data from 1972 to 1974 serves as a measurement point for present NO_2 air quality. For those stations with two or three years of data from 1972 to 1974, air quality indices are averaged over the two or three years. There are two advantages in using data from three years rather than from a single year. First, including more years increases the number of locations in the analysis. Second, averaging over two or three years, where possible, provides more robust estimates of the air quality indices.

Table 4.1 lists the 123 stations which have at least one year of complete data from 1972 to 1974. The arithmetic mean, 90th percentile,

Table 4.1 Stations for Characterizing Present NO_2 Air Quality

1. Phoenix, Arizona (002A01)
2. Anaheim, California (001I01
3. Azusa, California (002I01)
4. Bakersfield, California (003F01)
5. Barstow, California (001I01)
6. Burbank, California (002I01)
7. Camarillo, California (001I01)
8. Chico, California (001F01)
9. Chino, California (001I01)
10. Concord, California (001I01)
11. Costa Mesa, California (001I01)
12. El Cajon, California (001I01)
13. Eureka, California (002F01)
14. Fresno, California (002F01)
15. Indio, California (001I01)
16. La Habra, California (001I01)
17. Lancaster, California (001I01)
18. Lennox, California (001I01)
19. Livermore, California (002I01)
20. Long Beach, California (002I01)
21. Los Alamitos, California (001I01)
22. Los Angeles (Downtown), CA (001I01)
23. Los Angeles (Westwood), CA (002I01)
24. Los Angeles (Reseda), CA (001I01)
25. Lynwood, California (001I01)
26. Modesto, California (001I01)
27. Monterey, California (001I01)
28. Napa, California (003I01)
29. Newhall, California (001I01)
30. Norco, California (001I01)
31. Oakland, California (003G01)
32. Ojai, California (001I01)
33. Palm Springs, California (001I01)
34. Pasadena, California (004I01)
35. Pittsburgh, California (001I01)
36. Pomona, California (001I01)
37. Redding, California (002F01)
38. Redlands, California (001I01)
39. Redwood City, California (001I01)
40. Richmond, California (003I01)
41. Riverside, California (003F01)
42. Rubidoux, California (001I01)
43. Sacramento, California (003F01)
44. Salinas, California (001I01)
45. San Bernadino, California (001I01)
46. San Diego, California (004I01)
47. San Francisco, California (003I01)
48. San Jose, California (004A05)
49. San Luis Obispo, California (001F01)
50. San Rafael, California (001I01)
51. Santa Barbara, California (002F01)

Table 4.1 Stations for Characterizing Present NO_2 Air Quality (Continued)

52. Santa Barbara, California (004F01)
53. Santa Cruz, California (001I01)
54. Santa Rosa, California (002I01)
55. Stockton, California (002F01)
56. Sunnyvale, California (001I01)
57. Upland, California (003I01)
58. Upland, California (004F01)
59. Vallejo, California (003I01)
60. Victorville, California (001I01)
61. Visalia, California (001F01)
62. Whittier, California (001I01)
63. Yuba City, California (001F01)
64. Denver, Colorado (002A05)
65. New Britain, Connecticut (002F01)
66. Washington, D.C. (003A05)
67. Atlanta, Georgia (001A05)
68. Chicago, Illinois (002A06)
69. Chicago, Illinois (023A05)
70. Ashland, Kentucky (008F01)
71. Louisville, Kentucky (011G01)
72. Louisville, Kentucky (017A05)
73. Newport, Kentucky (001F01)
74. Ohio, Kentucky (006H02)
75. Owensboro, Kentucky (008F01)
76. Baltimore, Maryland (018F01)
77. Silver Spring, Maryland (006F01)
78. Springfield, Massachusetts (005A05)
79. Detroit, Michigan (020A05)
80. Lansing, Michigan (002F01)
81. Saginaw, Michigan (002F01)
82. Afton, Missouri (001G01)
83. Belle Fontaine Neighbors, Missouri (002G01)
84. Clayton, Missouri (001G01)
85. St. Ann, Missouri (001G01)
86. St. Louis, Missouri (002A10)
87. St. Louis, Missouri (006G01)
88. Las Vegas, Nevada (009G01)
89. Reno, Nevada (005I01)
90. Bayonne, New Jersey (003F01)
91. Camden, New Jersey (003F01)
92. Elizabeth, New Jersey (004F01)
93. Newark, New Jersey (002F01)
94. Phillipsburg, New Jersey (002F01)
95. Buffalo, New York (005F01)
96. Buffalo, New York (007F01)
97. Glens Falls, New York (003F01)
98. Hempstead, New York (005F01)
99. Kingston, New York (002F01)
100. Mamaroneck, New York (002F01)
101. New York City, New York (006A05)
102. New York City, New York (060F01)

Table 4.1 Stations for Characterizing Present NO_2 Air Quality (Continued)

103. New York City, New York
(061A05)

104. Niagara Falls, New York
(006F01)

105. Rensselaer, New York
(001F01)

106. Rochester, New York
(004F01)

107. Schenectady, New York
(003F01)

108. Syracuse, New York
(005F01)

109. Syracuse, New York
(011F01)

110. Utica, New York
(004F01)

111. Akron, Ohio
(013H01)

112. Cincinnati, Ohio
(019A05)

113. Portland, Oregon
(002F01)

114. Lancaster City, Pennsylvania
(007F01)

115. Philadelphia, Pennsylvania
(002A05)

116. Philadephia, Pennsylvania
(004H01)

117. Scranton, Pennsylvania
(006F01)

118. Providence, Rhode Island
(005F01)

119. Providence, Rhode Island
(007A05)

120. Memphis, Tennessee
(027N02)

121. Stewart, Tennessee
(005N02)

122. Salt Lake City, Utah
(001A05)

123. Alexandria, Virginia
(009H01)

yearly maximum, and ratio of yearly maximum to annual mean for each of the 123 stations can be found in Appendix C. The information in Appendix C will serve as the basis for characterizing present NO_2 air quality.

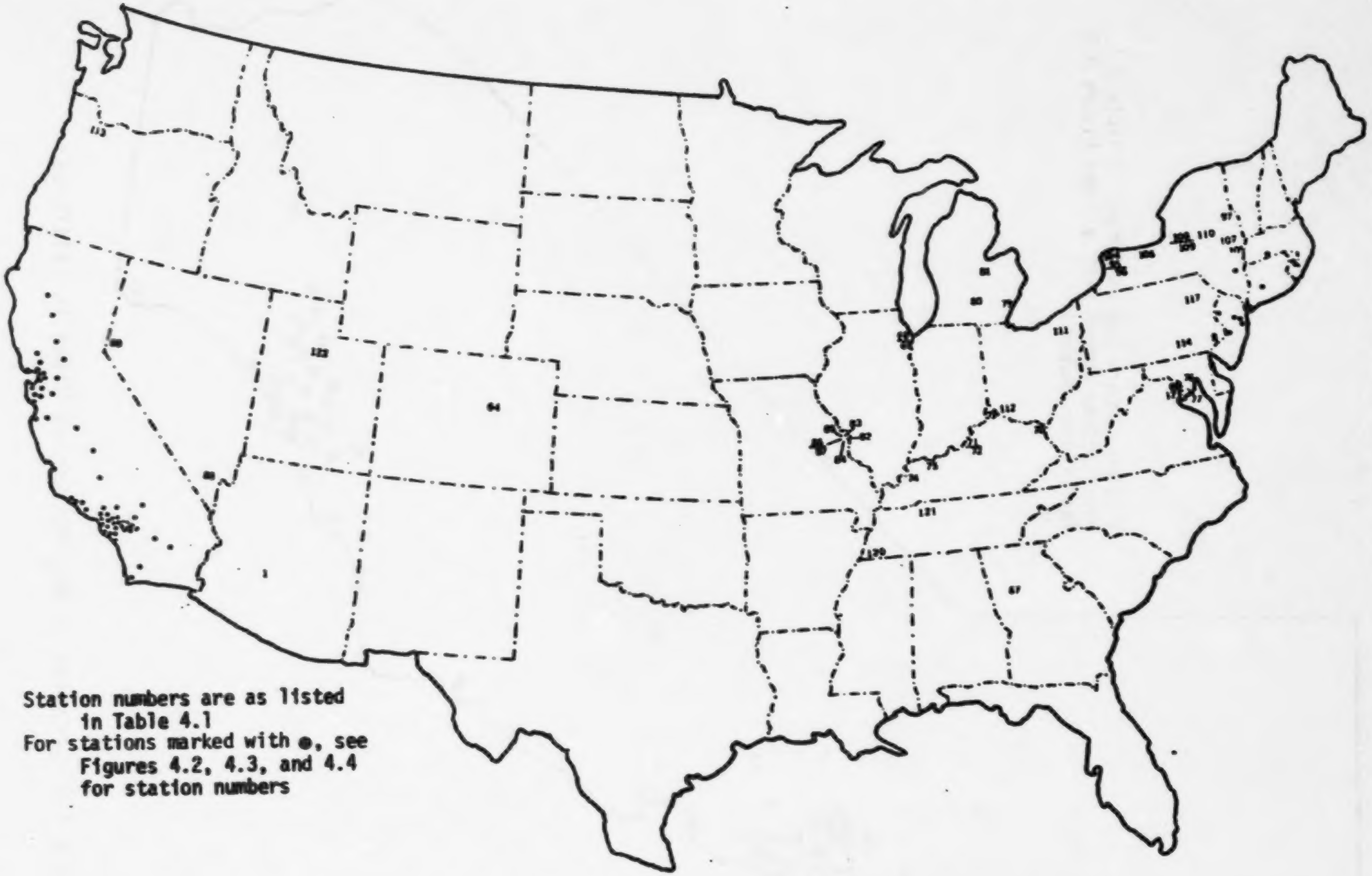
Figure 4.1 shows the locations of the stations on a map of the United States. Because of the high density of sites in California, the Los Angeles area, and the New York-New Jersey-New England region, separate maps are presented for those areas (see Figures 4.2 through 4.4). The numbers plotted on the maps correspond to the stations numbers listed in Table 4.1.

4.2 DATA PATTERNS INVOLVING MONITOR ENVIRONMENT

The SAROAD printout classifies the general environment of each monitor according to "center city," "suburban," and "rural." For the urban and suburban classes, a subcategorization can be made according to four local environments: commercial, industrial, residential, and mobile station. For the rural class, four other subcategories are possible: commercial, near urban, agricultural, and power plant. Table 4.2 indicates the distribution of the 123 sites among these categories.

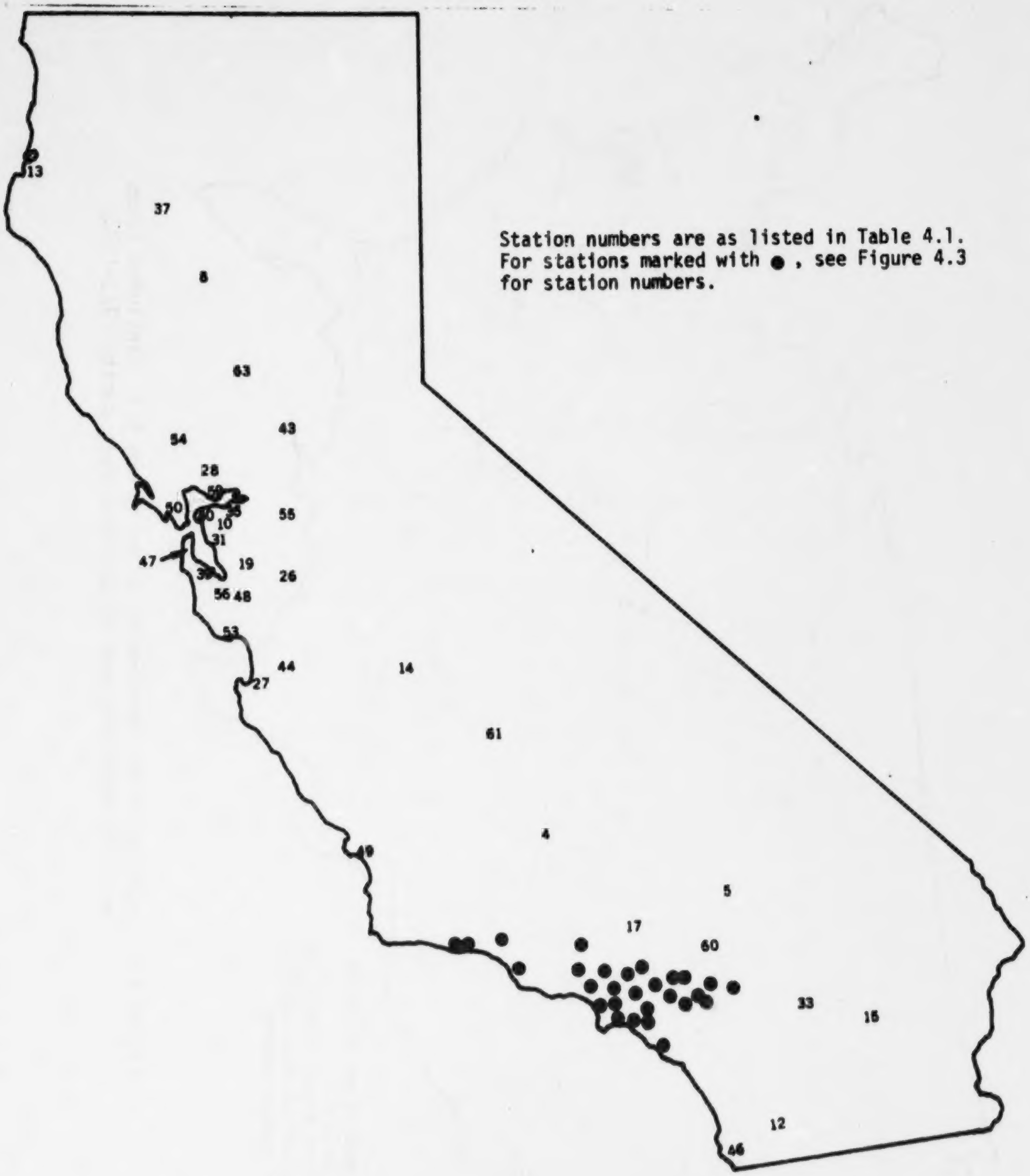
Table 4.2 Number of Sites in Various Categories of Monitor Environment

Center City		Suburban		Rural	
Commercial ...	57	Commercial ...	17	Commerical ...	1
Industrial ...	6	Industrial ...	7	Near Urban ...	1
Residential ...	9	Residential ...	17	Agricultural ...	1
Mobile ...	2	Mobile ...	2	Power Plant ...	3
Total	74	Total	43	Total	6


113
123
64
1
97
110
107
117
114
111
112
121
120
87
75

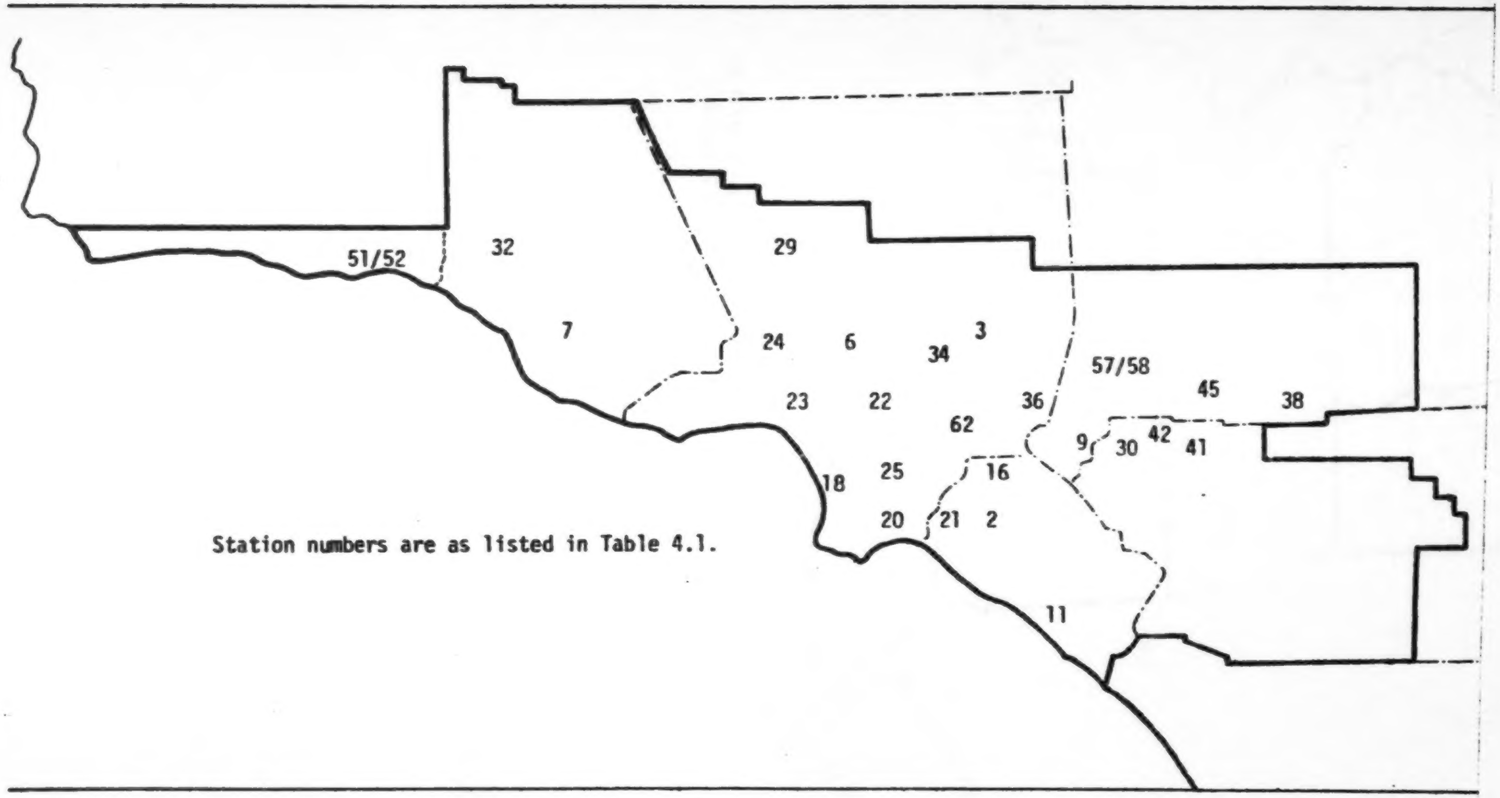
Station numbers are as listed
in Table 4.1
For stations marked with ●, see
Figures 4.2, 4.3, and 4.4
for station numbers

Figure 4.1 Location of NO_2 Monitoring Sites in the U.S. (Includes sites with at least one year of complete data during 1972-1974)


13
37
8
63
54
43
28
50
10
55
31
47
19
26
56
48
53
44
27
14
61
4
5
17
60
33
15
12
46

Station numbers are as listed in Table 4.1. For stations marked with ●, see Figure 4.3 for station numbers.

Figure 4.2 Location of NO_2 Monitoring Sites in California


51/52
32
7
29
24
6
34
3
23
22
62
36
57/58
45
38
9
30
42
41
18
25
16
20
21
2
11

Station numbers are as listed in Table 4.1.

Figure 4.3 Location of NO_2 Monitoring Sites in the Los Angeles Region

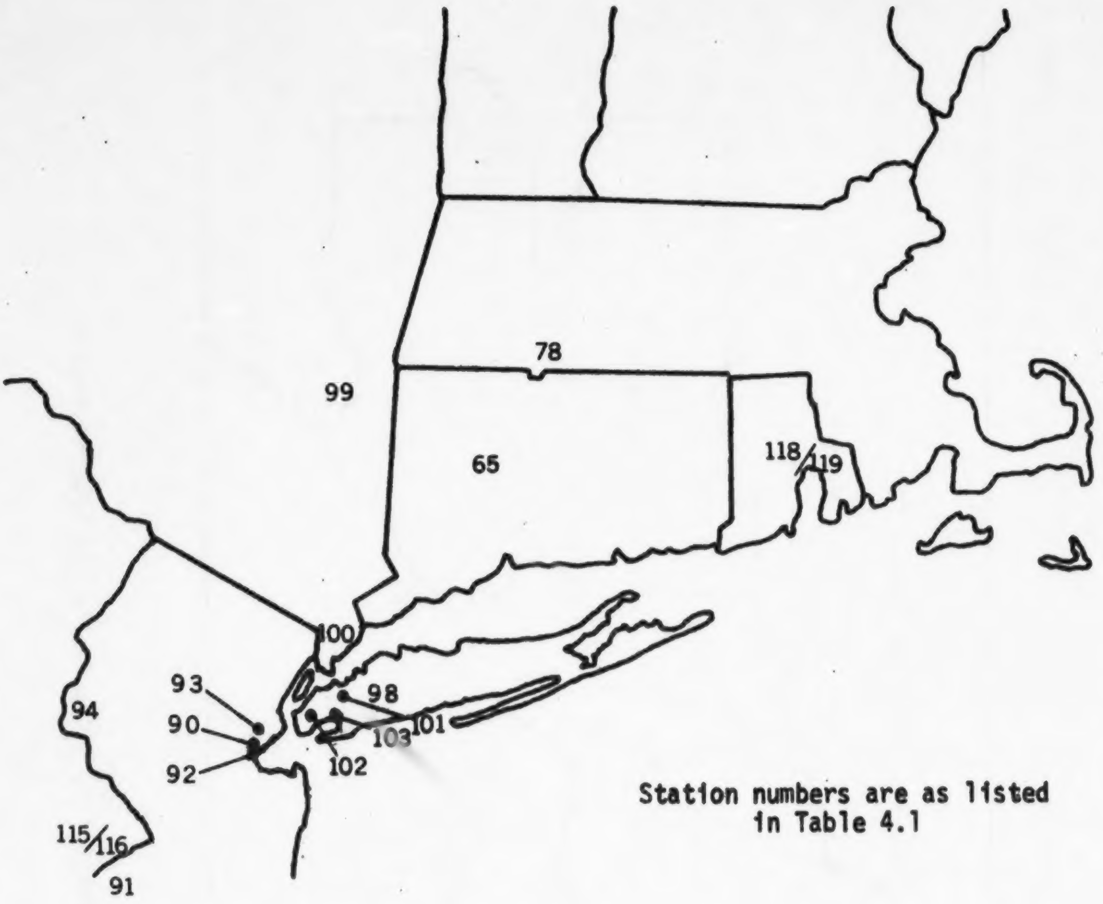

78
99
65
118/119
100
93
98
94
90
101
103
92
102
115/116
91
Station numbers are as listed in Table 4.1

Figure 4.4 Location of NO_2 Monitoring Sites in the New York-New Jersey-New England Area

It is interesting to determine if the different classifications of monitor environment are associated with different levels of NO_2 air quality. Table 4.3 lists average NO_2 air quality for each station classification. The only category of stations that stands out from the rest is the rural/power plant class. The three rural/power plant stations (Ohio Co.-Kentucky, Memphis-Tennessee, and Stewart Co.-Tennessee) exhibit very low annual means and 90th percentiles. The yearly maximum for these stations is only moderately low, leading to an extremely high ratio of yearly maximum to annual mean. This type of concentration distribution, low mean and a high maximum-to-mean ratio, is no surprise for these stations. The rural/power plant sites are subjected to near background NO_2 concentrations except for infrequent fumigation by power-plant plumes.

The most striking feature of the rest of the categories is their sameness. No substantial differences exist among the eight categories of center city and suburban stations. Even the three sites labeled as rural/commercial, rural/near urban, and rural/agricultural are not significantly different from the center city and suburban sites. Perhaps some of the uniformity is due to unrealistic classification. The rural/commercial site (Rubidoux, Ca.) and the rural/agricultural site (Norco, Ca.) are well inside the boundaries of the Los Angeles basin. The rural/near urban site is in St. Louis.

In the next section, maps will be presented which illustrate nationwide patterns in urban NO_2 air quality. These maps will be based on data

Table 4.3 NO_2 Air Quality for Various Categories of Monitor Environment

Type of Site	Number of Stations	Average NO_2 Air Quality for Station of Each Type (1972-1974)			
		Annual Mean (pphm)	90th Percentile (pphm)	Yearly Maximum (pphm)	Ratio of Maximum to Mean
Center City/ Commercial	57	3.5	6.2	23.6	6.7
Center City/Industrial	6	4.0	7.0	20.3	5.1
Center City/Residential	9	3.4	6.4	22.2	6.5
Center City/Mobile	2	3.0	5.2	13.8	4.6
Suburban/Commercial	17	4.3	7.8	27.8	6.5
Suburban/Industrial	7	4.1	7.6	24.5	6.0
Suburban/Residential	17	3.2	5.8	21.2	6.6
Suburban/Mobile	2	3.5	6.5	26.2	7.5
Rural/Commercial	1	2.7	5.0	20.3	7.5
Rural/Near Urban	1	3.0	6.0	33.6	11.2
Rural/Agricultural	1	2.8	5.0	22.4	8.0
Rural/Power Plant	3	0.8	1.3	14.4	18.0

from all 123 sites listed in Table 4.1, except for the 3 rural/power plant sites. The rural/power plant sites are atypical and will be treated separately. The 3 rural/commercial, rural/near urban, and rural/agricultural sites will be included among the urban locations.

4.3 NATIONWIDE GEOGRAPHIC PATTERNS IN NO_2 AIR QUALITY

The existing National Ambient Air Quality Standard (NAAQS) for nitrogen dioxide is $100 \mu g/m^3$ (approximately 5.3 pphm), annual arithmetic mean. If a short-term standard is promulgated for nitrogen dioxide, it may be a one-hour standard, or it may be based on a percentile concentration such as the 90th percentile. This section provides information which allows a comparison between present NO_2 air quality levels nationwide and the NAAQS, including the annual mean standard and potential one-hour or 90th percentile standards.

A drawback in characterizing nationwide air quality is the limited number of monitoring sites. During the 1972-to-1974 period, only 120 urban sites (58 outside California) provided 75% complete data on hourly NO_2 concentrations. As shown in Figure 4.1, the only areas of the country with good spatial coverage are California and the northeast sector (Illinois to New England). Thus, we cannot make definitive conclusions concerning the status of NO_2 air quality in all urban areas. We will, however, attempt to identify broad regions of the country with the potential for exceeding NO_2 air quality standards. A better assessment of nationwide air quality for nitrogen dioxide should be possible in the future as more stations come on line and as data quality improves from existing stations.

4.3.1 Annual Mean NO_2 Concentrations

Figure 4.5 illustrates the distribution of annual mean NO_2 concentrations for the 120 urban stations in the data base. Most of the stations have annual mean NO_2 concentrations in the range 1 pphm to 5 pphm. Only 18 of the stations, 15% of the total, exceed the NAAQS for annual mean NO_2 (5.3 pphm). Five of the 58 sites outside of California exceed the standard. Within California, 21% of the locations (13 out of 62) violate the standard; all of the California violations occur in the Metropolitan Los Angeles AQCR.

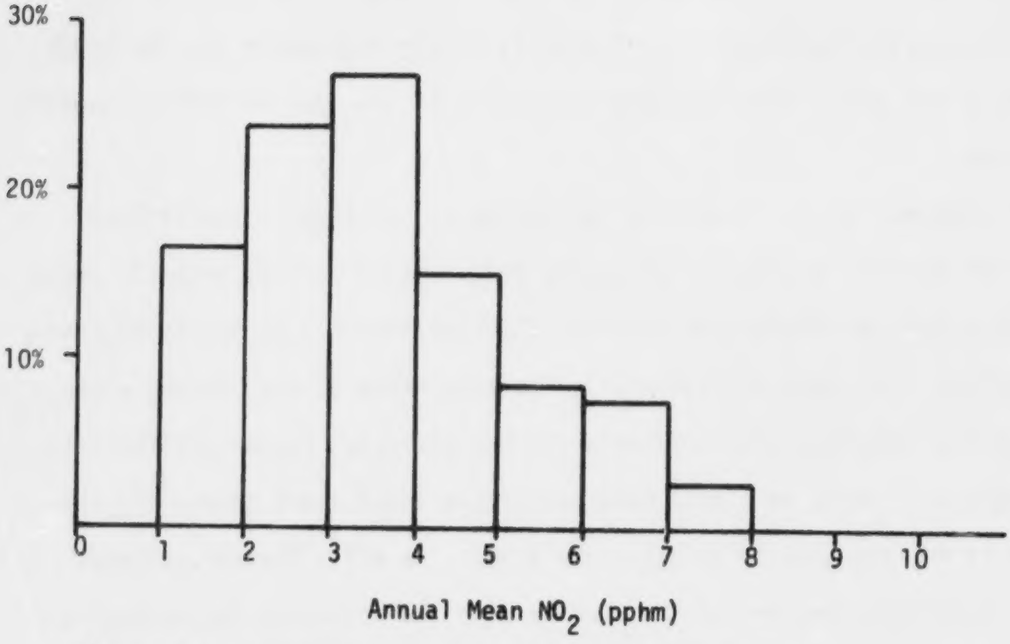


Figure 4.5 Percentage of Urban Stations with Various Levels of Annual Mean NO_2 Concentrations (1972-1974)

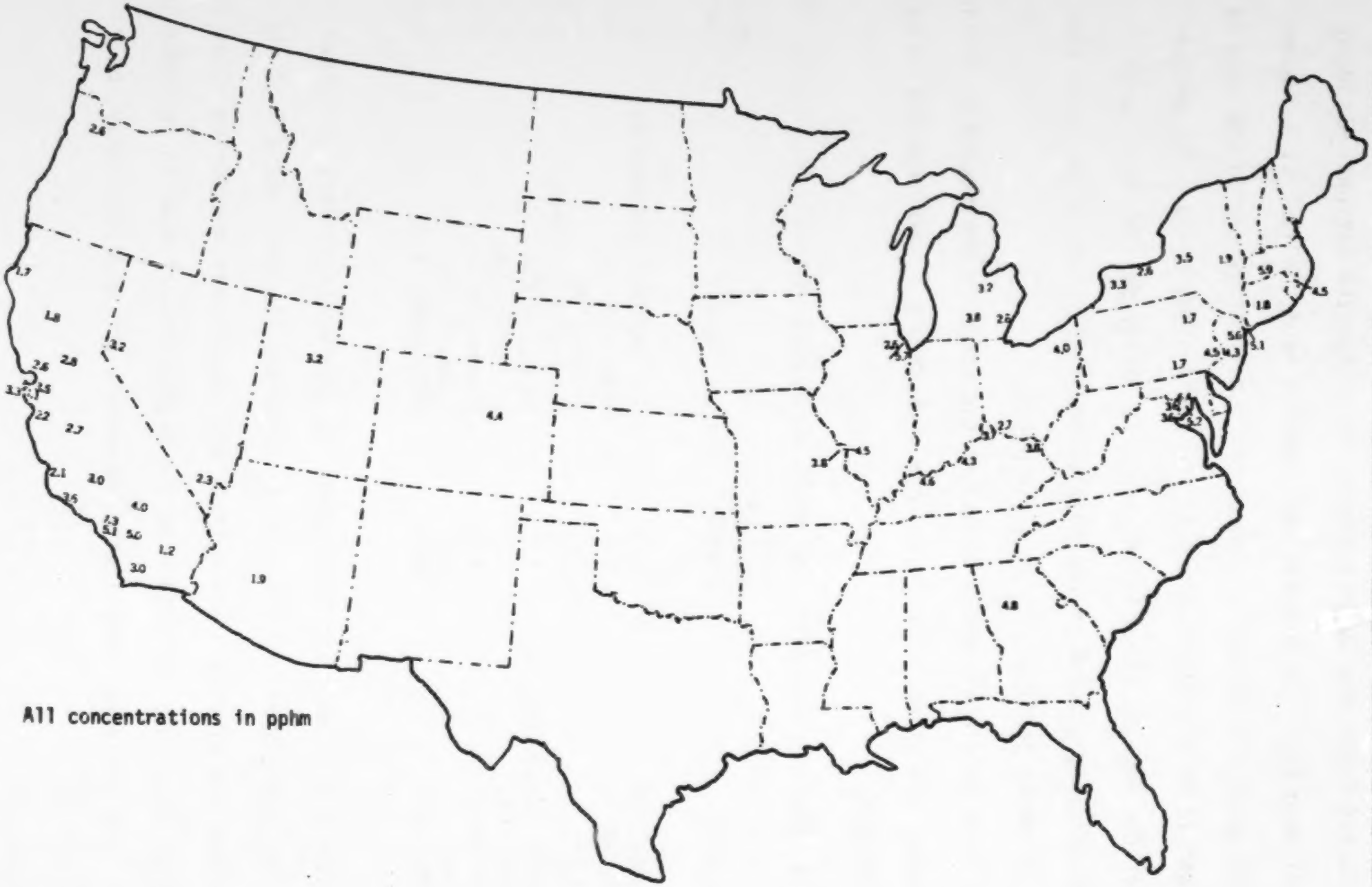
Table 4.4 lists the 18 locations which exceed the national standard for annual mean NO_2. Los Angeles and Pasadena head the list at 7.3 pphm, nearly 50% above the standard. Ten of the top 11 sites are in Los Angeles County, and 13 of the 18 sites are in the Los Angeles basin. The preponderance of Los Angeles sites in the table is partly due to the intense photochemical smog problem in Los Angeles and partly due to the large number of monitoring locations in that air basin.

The 5 non-California sites exceeding the standard are headed by Baltimore at 6.4 pphm. The other 4 non-California sites are all less than 20% in excess of the standard.

Table 4.4 Stations Exceeding the NAAQS for Annual Mean NO_2 (5.3 pphm), 1972-1974

Station	Mean NO_2 (pphm)	Station	Mean NO_2 (pphm)
Los Angeles, Ca.	7.3	Los Angeles (Reseda),Ca.	6.3
Pasadena, Ca.	7.3	Azusa, Ca.	6.2
Burbank, Ca.	7.1	Upland, Ca.	6.0
Pomona, Ca.	6.9	Springfield, Mass.	5.9
Los Angeles (Westwood),Ca.	6.8	Chicago, Ill.	5.7
Long Beach, Ca.	6.7	La Habra, Ca.	5.6
Whittier, Ca.	6.5	Newark, N.J.	5.6
Lennox, Ca.	6.4	Lynwood, Ca.	5.5
Baltimore, Md.	6.4	Elizabeth, N.J.	5.3

Figure 4.6 illustrates the nationwide geographic pattern of annual average NO_2 concentrations. To avoid cluttering the map, not all of the 120 stations are plotted. Where there are two or more monitoring sites in close proximity, only the site with the highest annual mean is included in the map. For instance, only 1 site represents Los Angeles County, only


2.6
1.7
1.8
3.2
2.6
2.8
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2.5
2.2
2.7
2.1
3.0
2.5
4.0
7.3
5.1
5.6
1.2
3.0
2.3
1.9
3.2
4.4
3.7
3.8
2.6
2.4
5.7
4.0
2.7
3.8
4.5
4.3
4.6
3.6
3.3
2.6
3.5
1.9
5.9
4.5
1.8
1.7
5.6
5.1
4.5
4.3
1.7
3.6
3.6
5.2
4.8

All concentrations in pphm

Figure 4.6 Annual Mean NO_2 Concentrations at Urban Stations in the United States (1972-1974)

4 sites represent the Los Angeles basin, 2 sites represent the St. Louis area, 1 site represents New York City, etc.

The Los Angeles area stands out in Figure 4.6 with the highest annual mean NO_2 concentration in the nation. Several cities in the Northeast and Chicago in the Midwest also exceed the NAAQS. None of the sites in the Southeast and none of the sites west of the Mississippi (except for Los Angeles) violates the federal standard, although Atlanta is close at 4.8 pphm. Because of the sparsity of stations in the Southeast and the West (except for California), we cannot be sure that the standard is attained everywhere in those areas. However, since some of the largest cities in those areas (such as Portland, Salt Lake City, Denver, Phoenix, and Atlanta) are represented, it seems unlikely that there would be significant violations among the unmonitored cities in the West and Southeast. The main problem areas in the nation with respect to attainment are Los Angeles and a few cities in the Northeast and Midwest.

4.3.2 90th Percentile NO_2 Concentrations

Figure 4.7 presents a histogram of 90th percentile NO_2 concentrations for the 120 stations in the data base. Most of the sites, 73% of the total, have 90th percentiles below 8 pphm. Only 14 sites, 12% of the total, have 90th percentile concentrations exceeding 10 pphm.

To point out the sites of the greatest NO_2 concentrations, Table 4.5 lists the 14 stations with 90th percentile concentrations that exceed 10 pphm. Eleven stations from the Los Angeles basin (10 from Los Angeles County) head the list. Of the other 3 sites, 2 are in Maryland, and 1 is in Massachusetts.

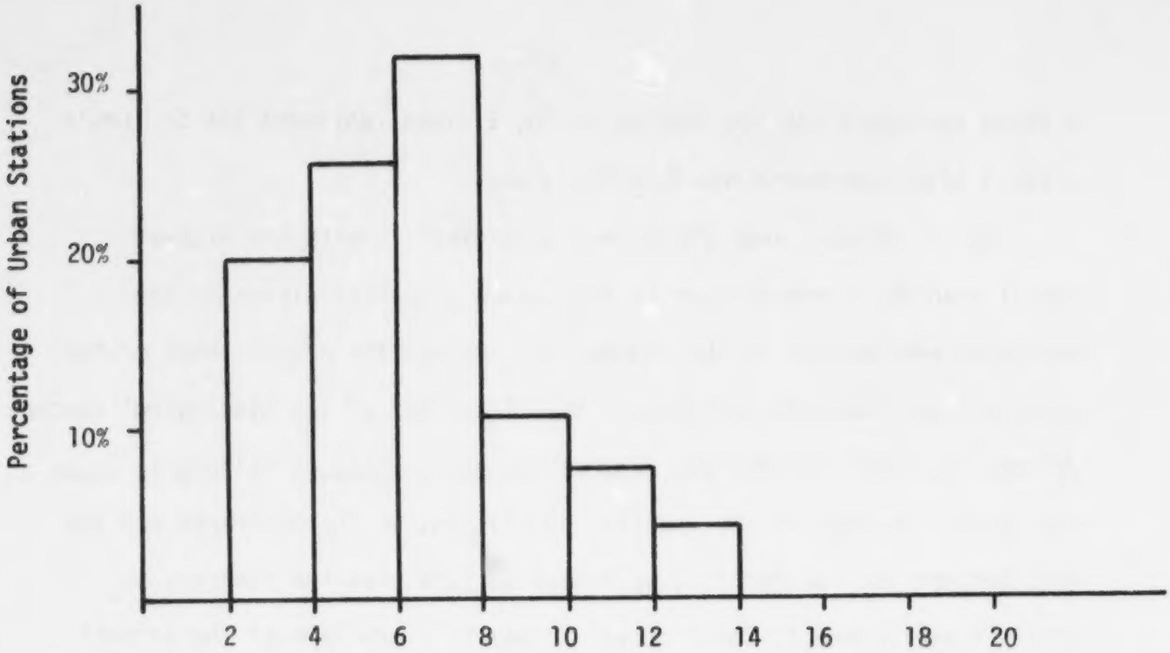
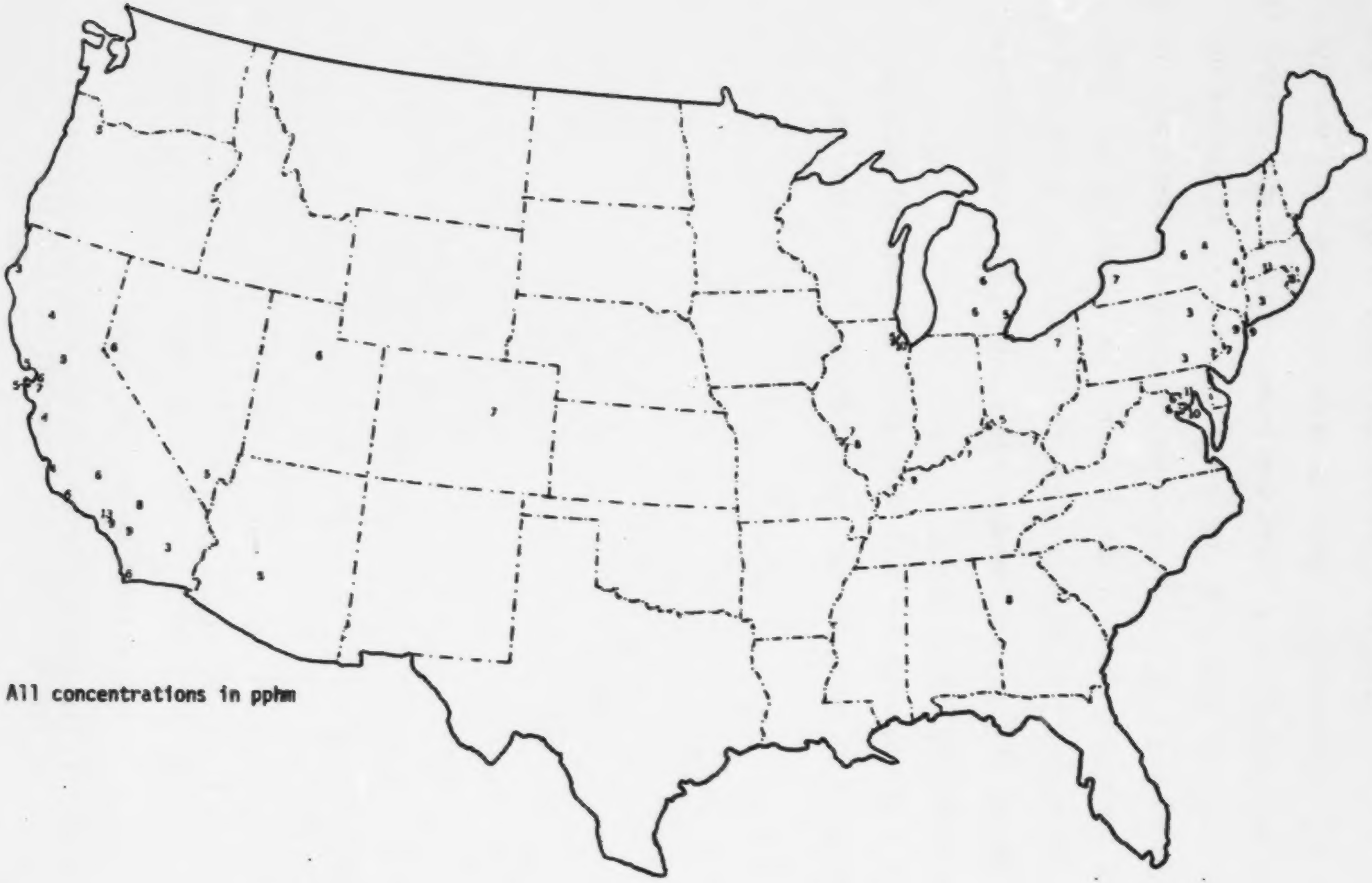


Figure 4.7 Percentage of Urban Stations with Various Levels of 90th Percentile Concentrations (1972-1974)

Table 4.5 Monitoring Sites with 90th Percentile NO_2 Concentrations Greater than 10 pphm (1972-1974)

Station	90th Percentile (pphm)	Station	90th Percentile (pphm)
Burbank, Ca.	13.0	Whittier, Ca.	11.3
Los Angeles, Ca.	12.3	Lennox, Ca.	11.0
Los Angeles (Westwood), Ca.	12.3	Pomona, Ca.	11.0
Pasadena, Ca.	12.0	Upland, Ca.	11.0
Long Beach, Ca.	12.0	Baltimore, Md.	11.0
Los Angeles (Reseda), Ca.	11.7	Springfield, Mass.	11.0
Azusa, Ca.	11.4	Silver Spring, Md.	10.0



All concentrations in pphm

Figure 4.8 90th Percentile NO_2 Concentrations at Urban Stations in the United States (1972-1974)

Figure 4.8 illustrates the nationwide geographic distribution of 90th percentile NO_2 concentrations. Again, to avoid cluttering, only the site with the highest 90th percentile is listed when there are two or more monitors in close proximity. The pattern in Figure 4.8 is similar to the pattern for annual means (Figure 4.6). Los Angeles has the highest concentrations in the nation, but the rest of the West has relatively low concentrations. A few cities in the Northeast and Midwest (Springfield, Baltimore, Silver Spring, New York, Newark, Chicago, and Owensboro) have notably high concentrations.

4.3.3 Yearly Maximal Concentrations

Figure 4.9 illustrates the distribution of yearly maximal one-hour concentrations of NO_2 among the 120 urban stations. Forty-seven of

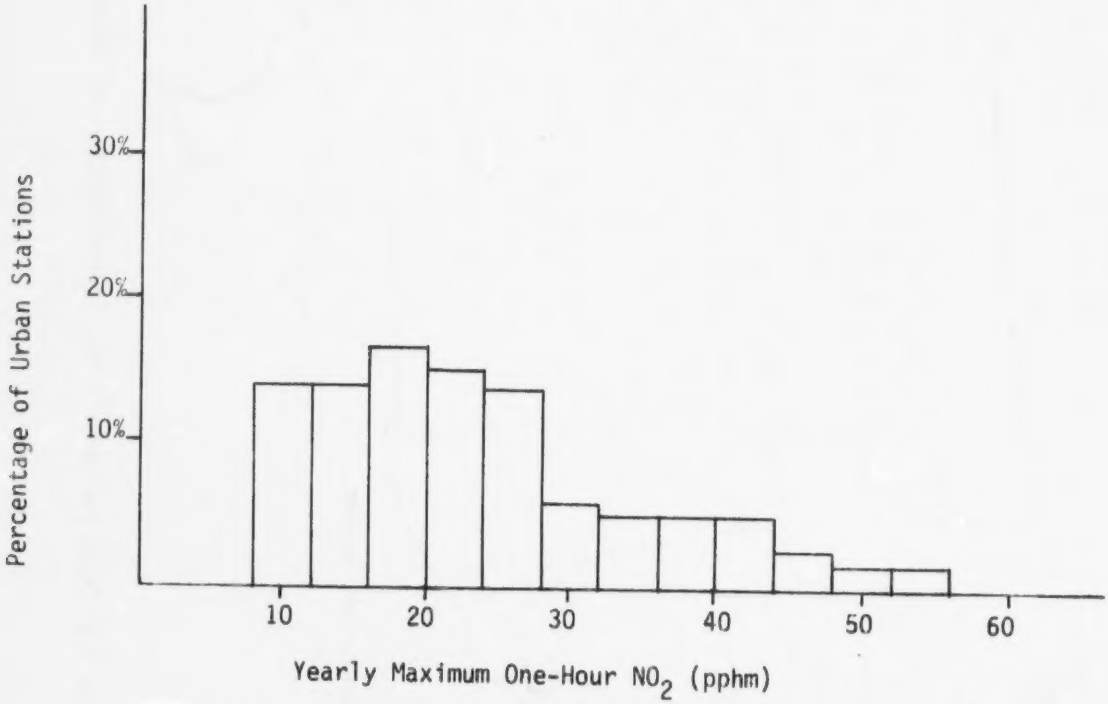


Figure 4.9 Percentage of Urban Stations with Various Levels of Yearly Maximum NO_2 Concentration (1972-1974)

the stations have yearly maxima which exceed 25 pphm (the California one-hour standard). Only 4 of the stations experience yearly maxima which exceed 50 pphm.

Table 4.6 lists the 19 stations with yearly NO_2 maxima exceeding 36 pphm. Again, the Los Angeles basin dominates the list; 4 of the top 5 and 14 of the top 19 locations are in the Los Angeles basin. Baltimore and Silver Spring, Maryland are also repeaters from the lists of "worst stations" for the annual mean and 90th percentile. Table 4.6 includes three other locations, Barstow, CA, Ashland, KY, and Denver, CO, that did not appear in Tables 4.4 or 4.5.

Table 4.6 Monitoring Sites with High Yearly Maximal One-Hour Concentrations (1972-1974)

Station	Yearly One-Hour Maximum (pphm)	Station	Yearly One-Hour Maximum (pphm)
Los Angeles (Westwood), CA	55.8	Anaheim, CA	40.7
Los Angeles, CA	54.6	Lennox, CA	40.7
Baltimore, MD	51.9	Denver, CO	40.2
Whittier, CA	50.6	Upland, CA	39.7
Pasadena, CA	47.7	Long Beach, CA	37.7
Barstow, CA	47.7	Lynwood, CA	37.7
Silver Spring, MD	45.1	Chino, CA	37.7
La Habra, CA	42.9	Los Angeles (Reseda), CA	36.7
Ashland, KY	41.6	Los Alamitos, CA	36.3
Azusa, CA	41.0		

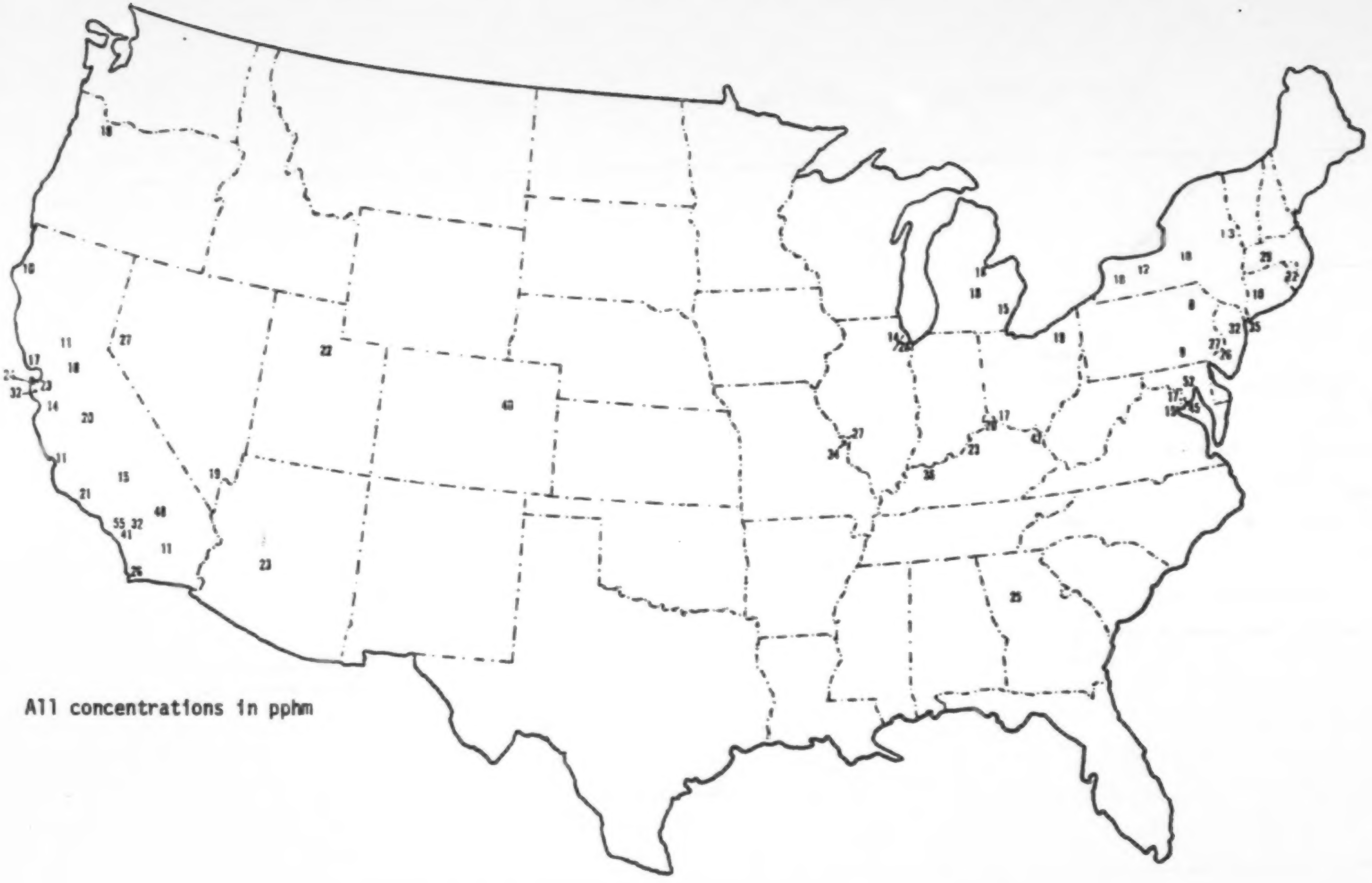
Figure 4.10 shows the nationwide geographic distribution of yearly maximal NO_2 concentrations. Only the station with the highest yearly maximum is listed on the map when there are several stations in close proximity. Los Angeles again stands out as having the greatest NO_2 concentrations in the country. The Baltimore area also appears as a "hot-spot". Other areas with high maximal NO_2 concentrations include Denver, CO, Ashland, KY, Owensboro, KY, and New York City.

4.4 INTRAREGIONAL PATTERNS IN NO_2 CONCENTRATIONS

There are at most four regions in the country where the monitoring sites in our data base are sufficiently dense to describe spatial patterns of NO_2 concentrations within the region. These regions are the Los Angeles basin, the San Francisco Bay area, the St. Louis region, and the New York-New Jersey-New England area. Two of these areas, Los Angeles and New York, are particularly interesting because they exceed the NAAQS for annual mean NO_2. Intraregional patterns for the Los Angeles and New York will be discussed below.

4.4.1 Metropolitan Los Angeles AQCR

Figure 4.11 presents a map of the Metropolitan Los Angeles region. The map shows the six counties that are within or partially within the region. It also notes the location of major cities in the region. When analyzing air pollution in the Los Angeles region, it is important to note that the area


18
10
11
27
17
18
23
32
14
20
11
15
19
21
48
55
32
41
11
26
22
23
40
27
34
14
20
16
18
15
17
20
23
38
42
18
18
17
18
13
25
22
18
8
32
25
27
26
9
32
17
19
15
25

All concentrations in pphm

Figure 4.10 Yearly One-Hour Maximum Concentrations at Urban Stations in the United States (1972-1974)

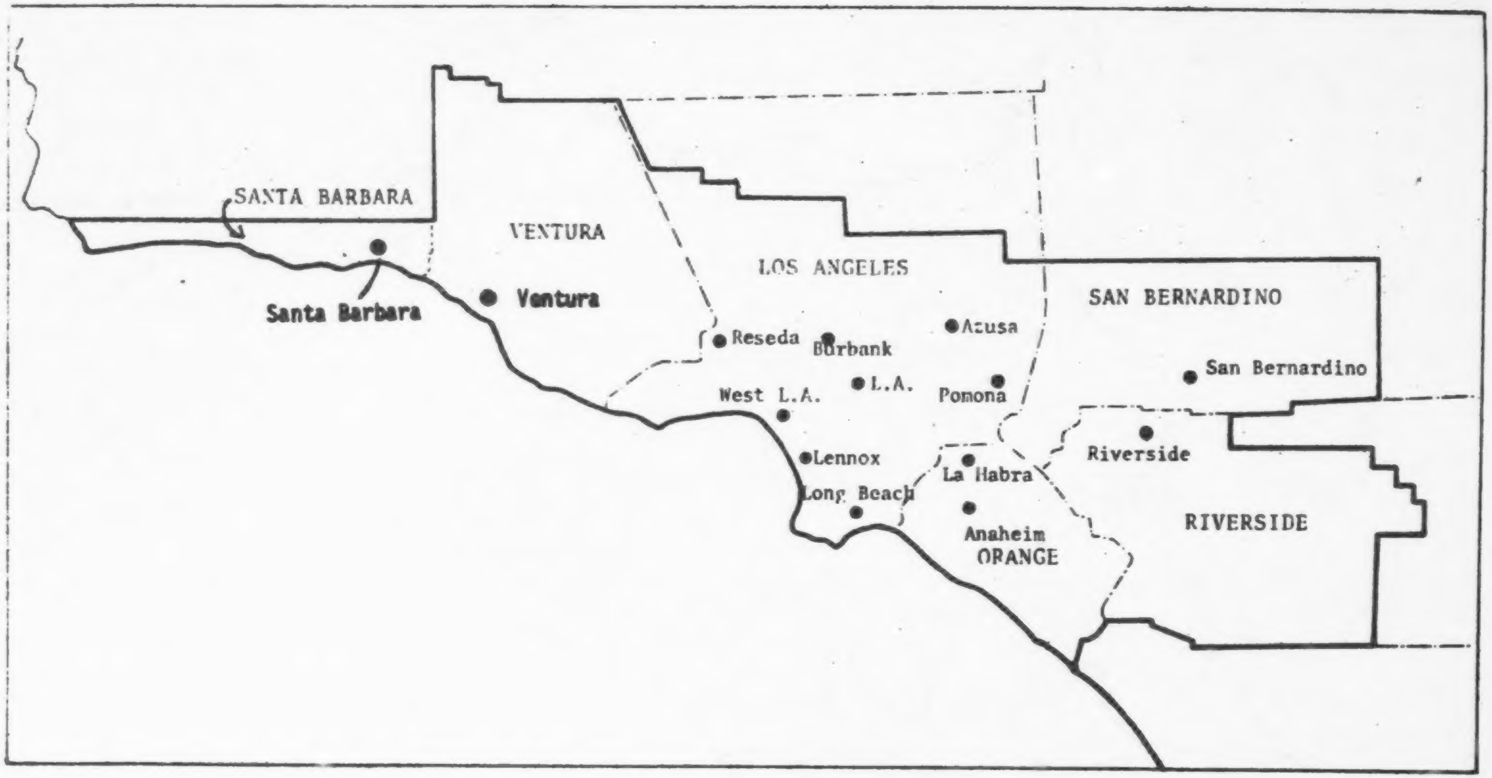

SANTA BARBARA
Santa Barbara
VENTURA
Ventura
LOS ANGELES
Reseda
Burbank
Azusa
West L.A.
L.A.
Pomona
Lennox
Long Beach
La Habra
Anaheim
ORANGE
SAN BERNARDINO
San Bernardino
Riverside
RIVERSIDE

Figure 4.11 Map of the Metropolitan Los Angeles AQCR

of highest traffic density and greatest industrial/commercial activity is the central/coastal area. This is demonstrated in Figure 4.12 [1], which shows the distribution of NO_x emissions within the region; a major portion of regional emissions occur in the western/central parts of Los Angeles County. It is also important to recognize that the meteorology of Los Angeles is dominated by a daytime sea breeze during much of the year. Typically, there is a transport of air pollutants from the coast toward the inland areas. Dilution occurs along with the transport. It is noteworthy that mixing heights are lowest at the coast and greatest inland.

Figures 4.13, 4.14, and 4.15 illustrate the spatial patterns of NO_2 concentrations within the Los Angeles basin. The three figures are for annual mean, 90th percentile, and yearly maximum concentrations, respectively. The patterns in all three figures are similar. The greatest NO_2 concentrations occur in the area of greatest NO_x emission density, i.e., the coastal and central parts of Los Angeles County. The stations at Westwood, Downtown, Pasadena, and Burbank show particularly high concentrations. The eastern/inland stations show moderately high concentrations, while the Ventura and Santa Barbara stations record relatively low concentrations.

Figures 4.13 through 4.15 indicate that the NO_2 problem in Los Angeles is partly regional in nature. Stations such as Azusa, Pomona, and Upland that are directly downwind of the most source-intensive area experience fairly high concentrations even though they are located in areas of relatively low emission density. Stations which rarely experience transport from the central areas, such as Santa Barbara or Ventura County stations, show the lowest concentrations. There is also evidence that the NO_2 problem is partly

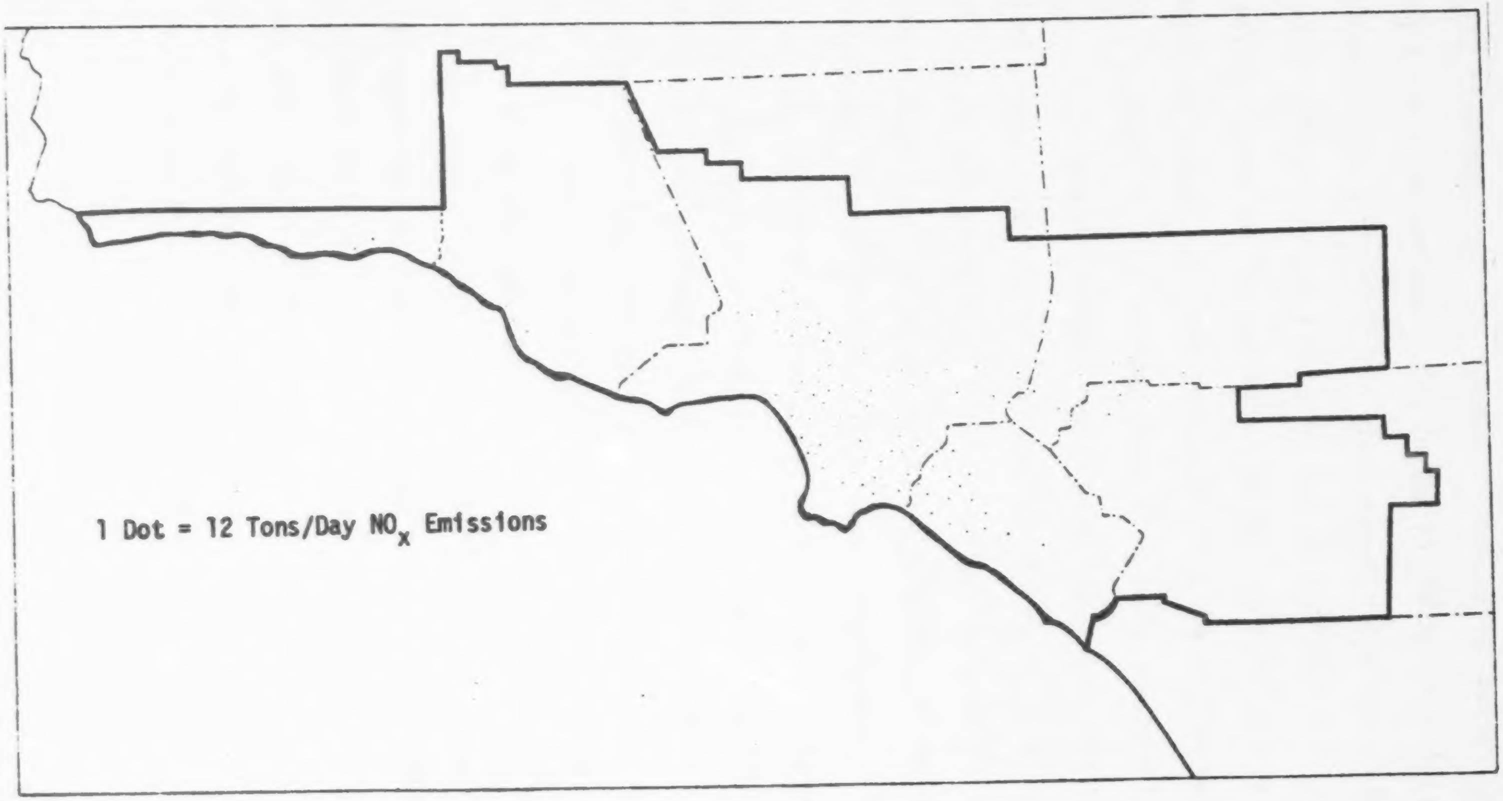
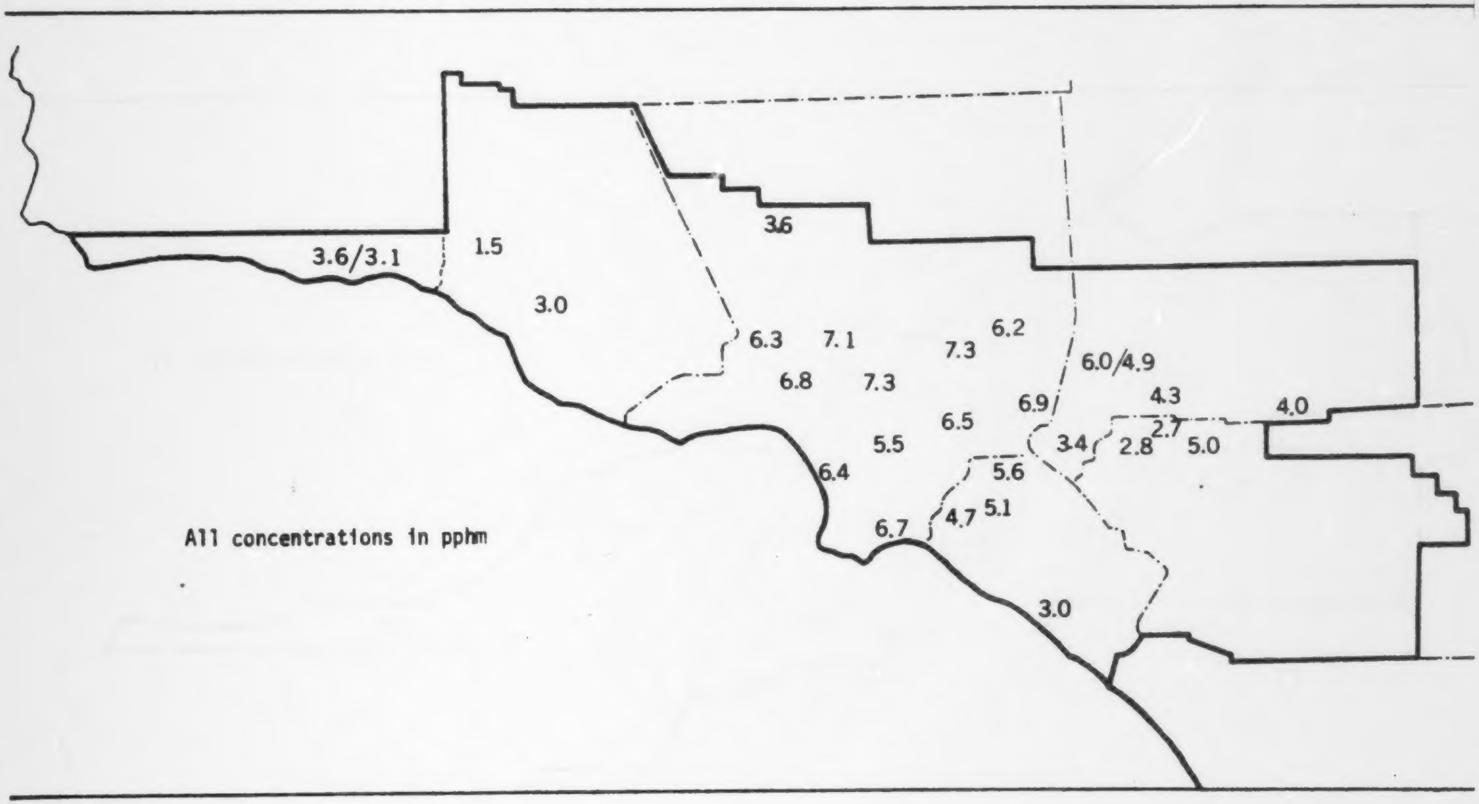

1 Dot = 12 Tons/Day NO_x Emissions

Figure 4.12 Nitrogen Oxides Emission Density Map for the Los Angeles Region
Source: Reference [1]


3.6/3.1
1.5
3.0
3.6
6.3
7.1
6.8
7.3
7.3
6.2
6.5
5.5
6.4
6.7
6.9
6.0/4.9
4.3
4.0
3.4
2.8
2.7
5.0
5.6
5.1
4.7
3.0

All concentrations in pphm

Figure 4.13 Annual Mean NO_2 Concentrations in the Los Angeles Region (1972-1974)

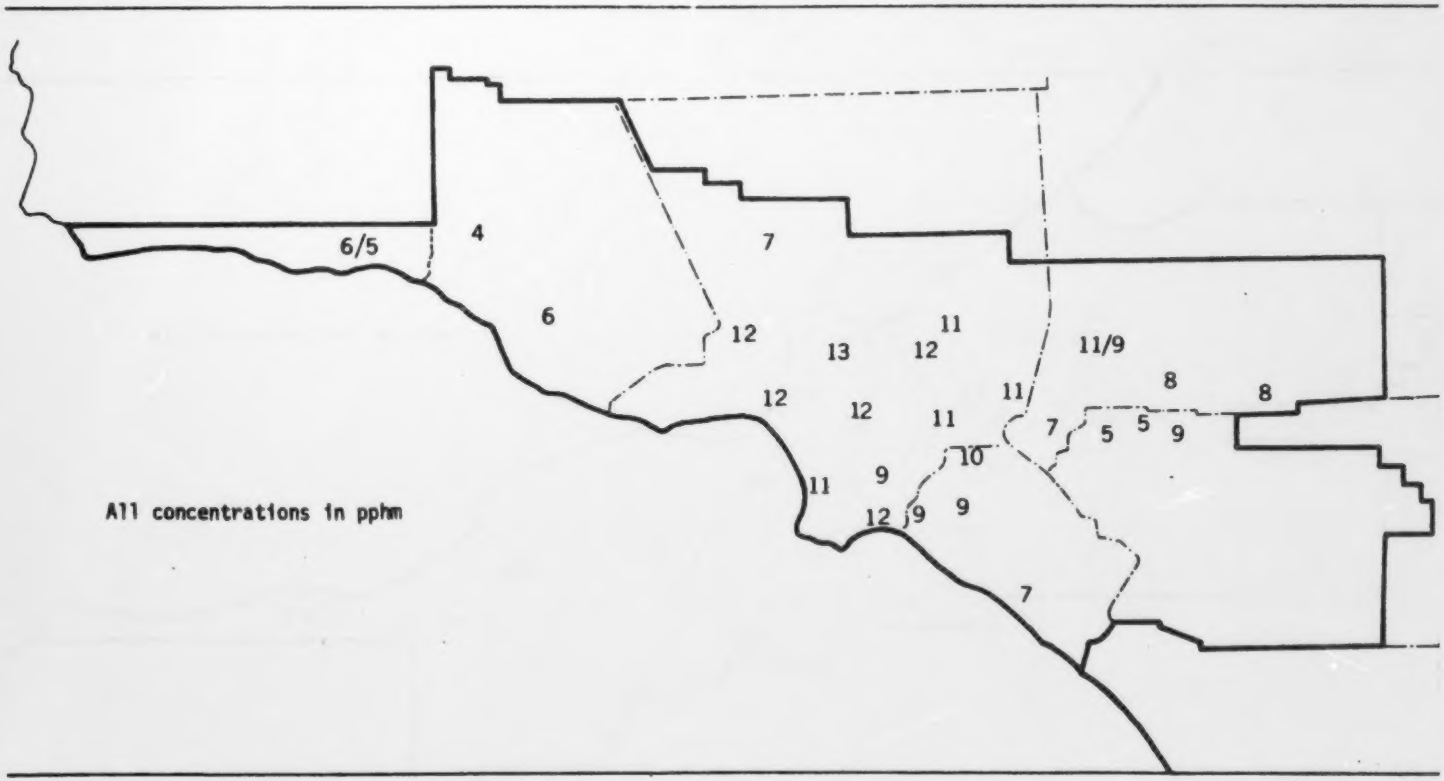

6/5
4
6
7
12
13
12
11
11/9
8
8
12
12
11
11
7
5
5
9
10
11
9
12
9
9
7
All concentrations in pphm

Figure 4.14 90th Percentile NO_2 Concentrations in the Los Angeles Region (1972-1974)

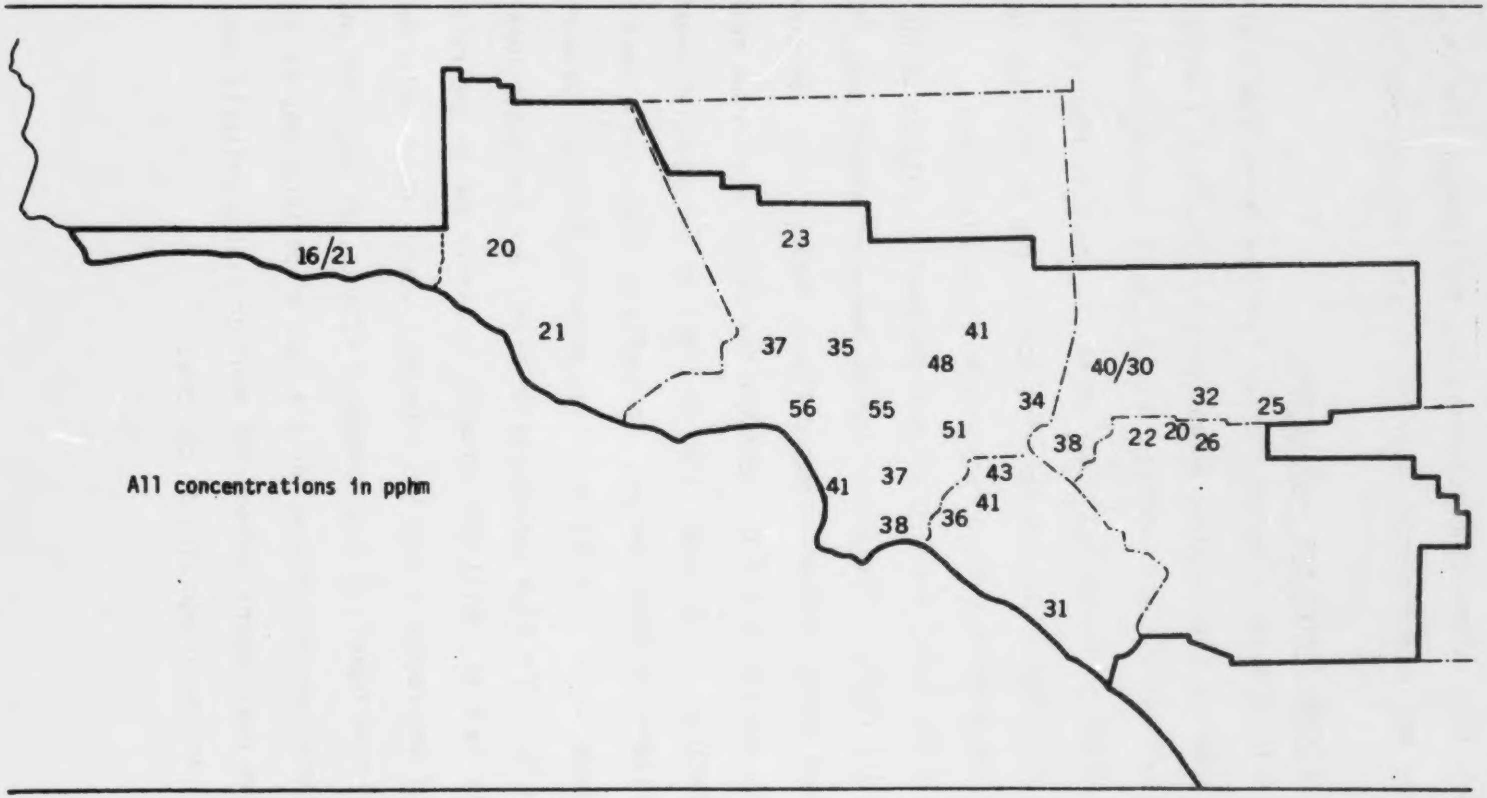

16/21
20
21
23
37
35
41
48
56
55
51
34
40/30
32
25
38
22
20
26
43
41
37
41
38
36
31
All concentrations in pphm

Figure 4.15 Yearly One-Hour Maximum NO_2 Concentrations in the Los Angeles Region (1972-1974)

localized in nature. Norco and Rubidoux in Riverside County show lower concentrations than surrounding stations, and the Lynwood site in Los Angeles County has significantly lower NO_2 levels than adjacent stations.

4.4.2 New York-New Jersey-New England Area

Figure 4.16 presents a map of the New York-New Jersey-New England area. This area has been studied extensively by Cleveland, Kleiner, and their associates at Bell Laboratories [2,3,4,5]. An NO_x emission density map, prepared by the Bell Labs group, is shown in Figure 4.17. The most striking feature of the emission density map is the high level of emissions in the northeast New Jersey and New York City areas.

Figures 4.18, 4.19, and 4.20 present the spatial pattern of NO_2 concentrations for the region. The three figures represent annual mean, 90th percentile, and yearly maximum concentrations, respectively. On each of the three figures, the New York City/ northern New Jersey area shows relatively high concentrations. This makes sense in light of the emission density map. No other consistent patterns emerge. Springfield, Mass. has a very high annual mean, even though it is in a region of low emission density. Between Springfield and New York (the high-concentration sites) are two exceptionally clean stations. The lack of consistent patterns is partly due to the relatively large scale of the region (~ 500 km). On this scale, local emissions are probably much more important than transport effects, at least for nitrogen dioxide. Another possible reason for the lack of patterns may be inconsistencies between measurement methods and monitor siting criteria used by the various state and local agencies in the area.

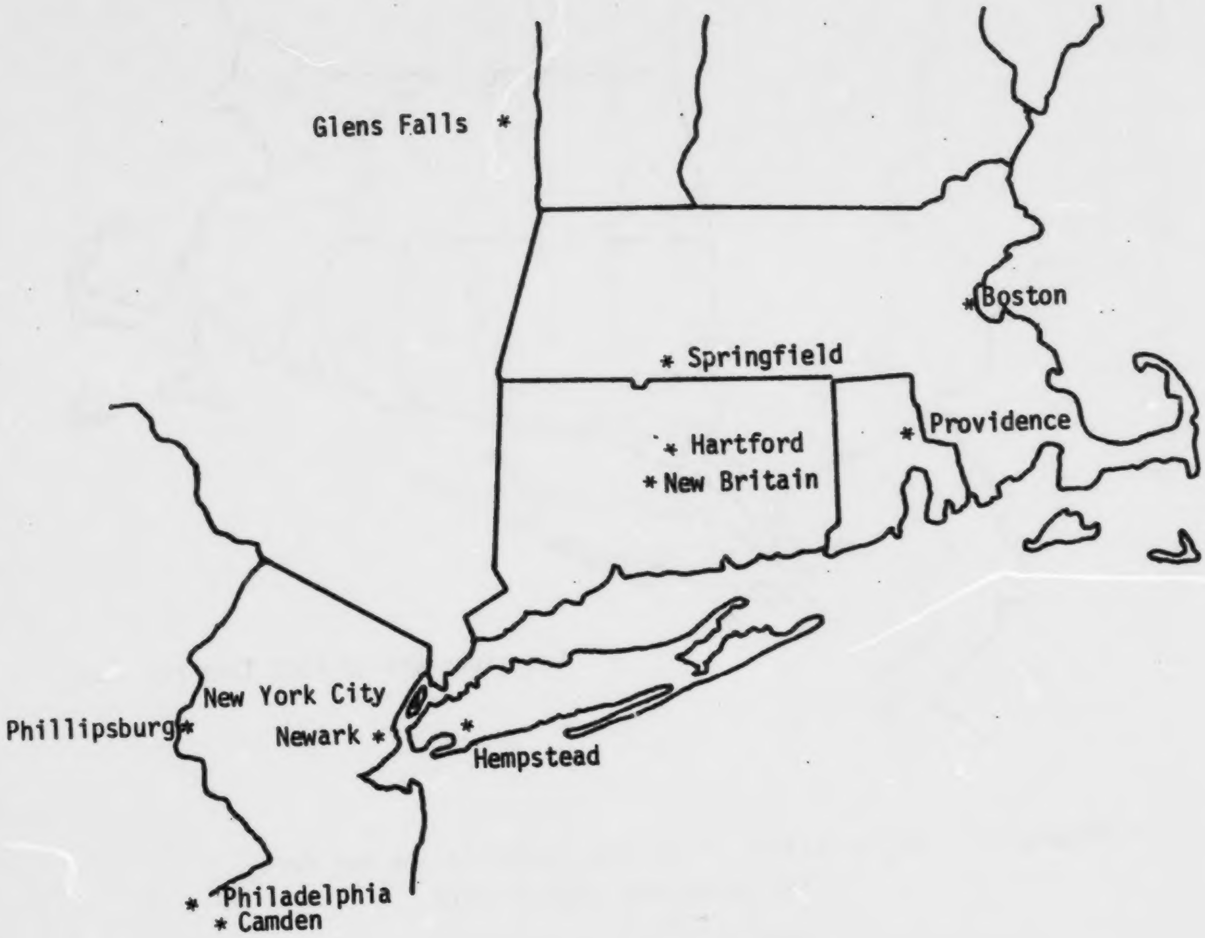

Glens Falls
Boston
Springfield
Providence
Hartford
New Britain
New York City
Phillipsburg
Newark
Hempstead
Philadelphia
Camden

Figure 4.16 Map of the New York-New Jersey-New England Area

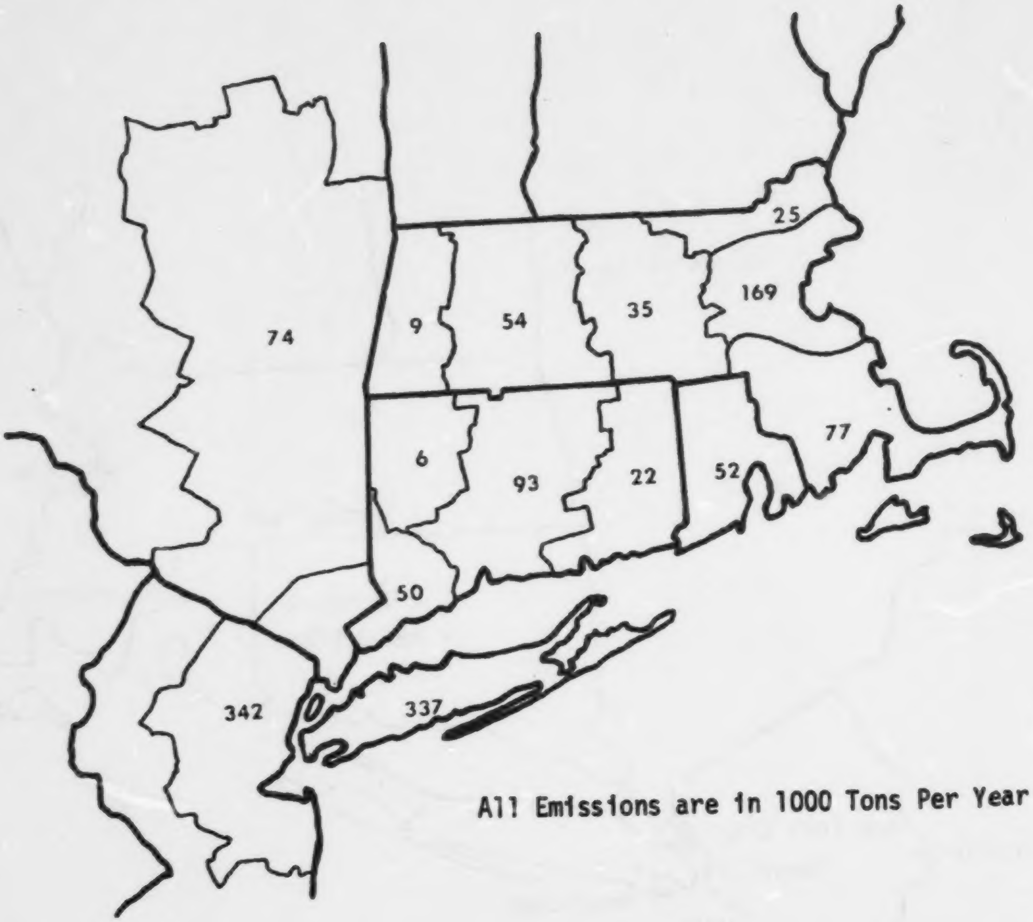

74
9
54
35
25
169
6
93
22
52
77
50
342
337
All Emissions are in 1000 Tons Per Year

Figure 4.17 NO_X Emissions in Various AQCRs in the New York-New Jersey-New England Area

Source: Reference [5]

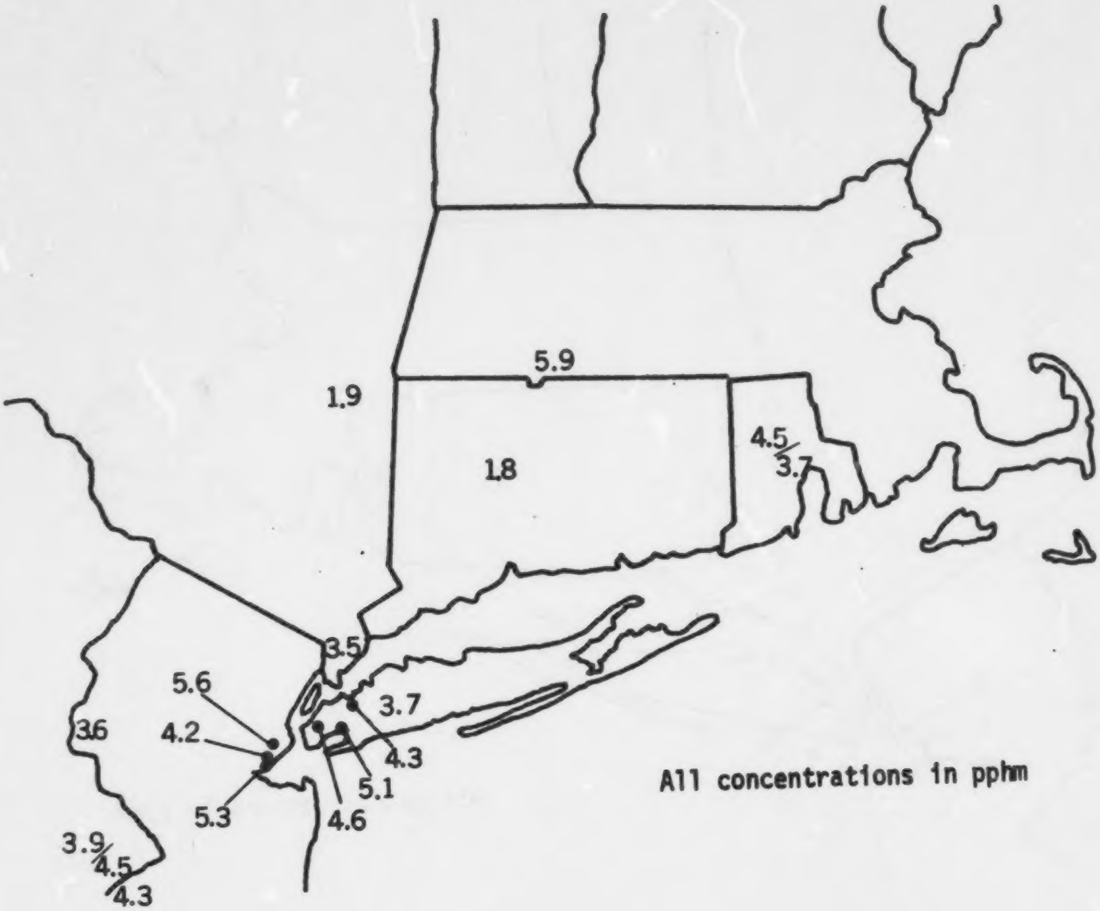
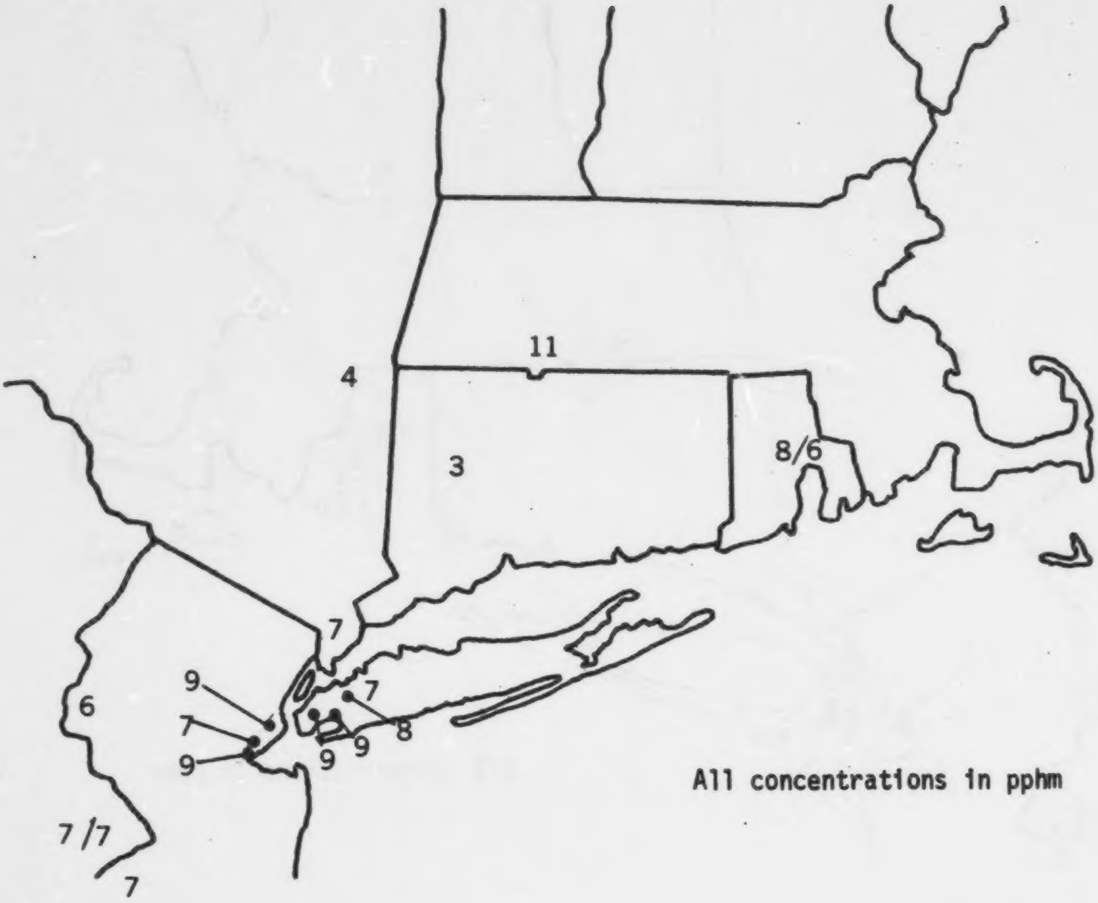

5.9
1.9
1.8
4.5
3.7
3.5
5.6
3.7
3.6
4.2
4.3
5.1
5.3
4.6
3.9
4.5
4.3
All concentrations in pphm

Figure 4.18 Annual Mean NO_2 Concentrations in the New York-New Jersey-New England Area (1972-1974)



11
4
3
8/6
7
9
7
6
7
8
9
9
9
7 /7
7
All concentrations in pphm

Figure 4.19 90th Percentile NO_2 Concentrations in the New York-New Jersey-New England Area (1972-1974)

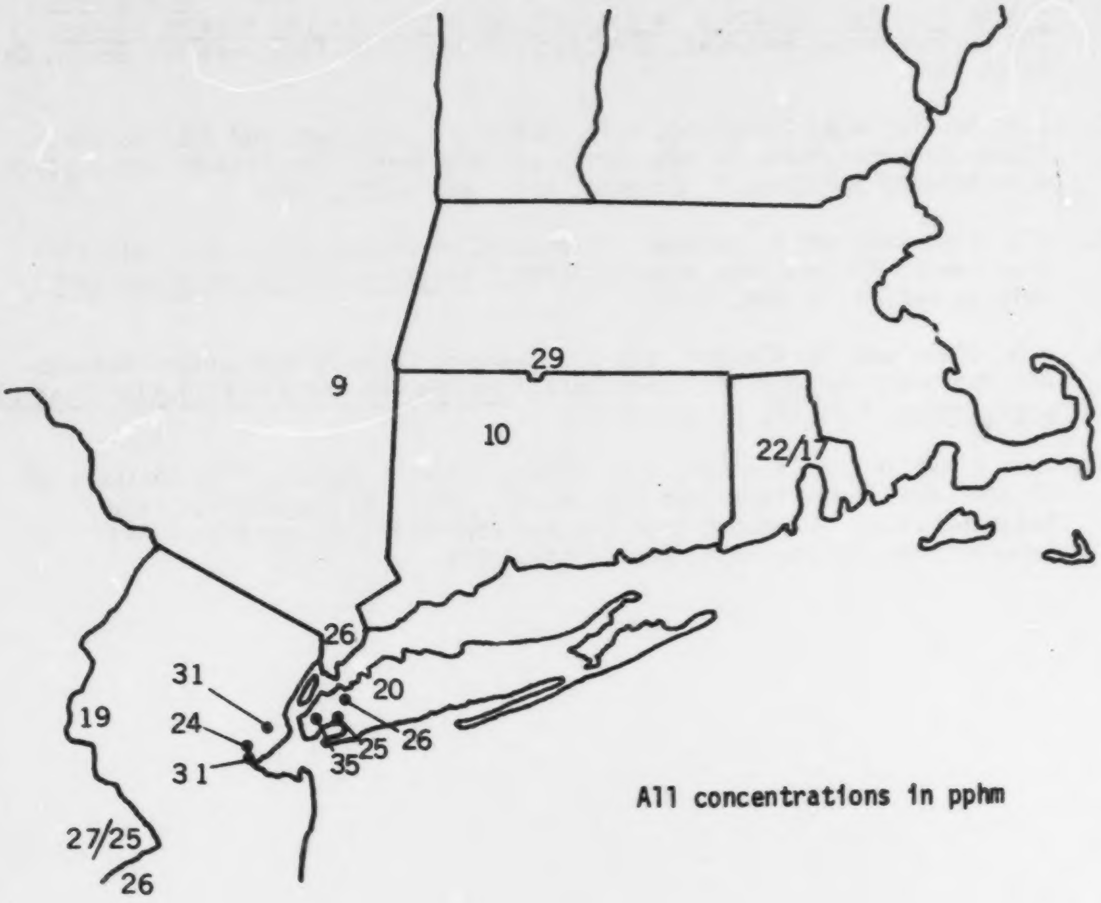

29
9
10
22/17
26
31
20
19
24
26
25
35
3 1
27/25
26
All concentrations in pphm

Figure 4.20 Yearly One-Hour Maximum NO_2 Concentrations in the New York-New Jersey-New England Area (1972-1974)

4.5 REFERENCES

1. J. Trijonis, G. Richard, K. Crawford, R. Tan, and R. Wada. An Implementation Plan for Suspended Particulate Matter in the Los Angeles Region, TRW Environmental Services, EPA Contract No. 68-02-1384, Redondo Beach, Ca., March 1975.

2. S.M. Bruntz, W.S. Cleveland, T.E. Graedel, B. Kleiner, and J.L. Warner, "Ozone Concentrations in New Jersey and New York: Statistical Association with Related Variables," Science, Vol. 186, p.257, 1974.

3. W.S. Cleveland and B. Kleiner, "Transport of Photochemical Air Pollution from Camden-Philadelphia Urban Complex," Environmental Science and Technology, Vol. 9, p. 869, 1975.

4. W.S. Cleveland, B. Kleiner, and J.L. Warner, "Robust Statistical Methods and Photochemical Air Pollution Data," Journal of the Air Pollution Control Association, Vol. 26, p. 36, 1976.

5. W.S. Cleveland, B. Kleiner, J.E. McRae, and J.L. Warner, "The Analysis of Ground-Level Ozone Data from New Jersey, New York, Connecticut, and Massachusetts: Transport from the New York Metropolitan Area," Bell Laboratories, Murray Hill, New Jersey, 1975.

5.0 TRENDS IN NITROGEN DIOXIDE AIR QUALITY

This chapter examines recent historical trends in ambient NO_2 concentrations. As in the previous chapter, the focus is on three air quality indices: annual mean, 90th percentile, and yearly one-hour maximum. Five- and ten-year changes in NO_2 concentrations are examined, using the data base described in Chapter 2. Year-to-year trends are investigated with an expanded data base. The year-to-year trends are discussed in terms of emission-factor changes and source growth.

5.1 FIVE- AND TEN-YEAR CHANGES IN NO_2 AIR QUALITY

A convenient way of determining overall air quality trends is to fit a regression line to the year-to-year levels of air quality. The change in ambient concentrations over a period of interest is defined by the values of the regression line at the beginning and end of the period. This method is applied here to determine net changes in NO_2 concentrations for individual stations over the periods 1969-1974 and 1964-1974.

The data base described in Chapter 2 serves as the basis for this trend study. To ensure adequate data for the trend estimates, five-year trends are determined only for those stations with at least two years of complete data from 1969 to 1971 and at least two years of complete data from 1972 to 1974. Ten-year trends are computed only for those stations with at least three years of complete data from 1964 to 1968 and at least three years of complete data from 1970 to 1974. For a given location, data are included only if they have been taken with the same monitoring method each year. Stations are excluded from the analysis if the site has been relocated or if there has been a change in the monitoring agency. With these restrictions, 19 sites in the data base qualify for the five-year trend analysis, and 10 sites qualify for the ten-year analysis.

Table 5.1 summarizes five-year trends at various monitoring sites. Net percentage changes in annual mean, 90th percentile, and yearly maximum NO_2 concentrations are listed for each site. The sites are grouped according to geographical area.

Caution should be followed in drawing inferences from five-year trend estimates. Year-to-year meteorological variance can play havoc with air quality trends over a span of five years. Substantially different results occur, depending on whether the first (or last) couple of years were good years for air quality or bad years. With the 90th percentile concentrations there is an additional problem, round-off error. For most locations, the percentile concentrations are reported only to the nearest pphm, and the error in round-off can be significant. The large upward trend in 90th percentile concentrations at Portland may, in part, be due to this type of error. The reported 90th percentiles at Portland from 1970 to 1974 are 4, 4, 4, 5, and 5 pphm, respectively.

With these caveats in mind, we make the following observations concerning five-year trends. Essentially no overall change in NO_2 concentrations occurred in Los Angeles County over the five years. Orange County, a rapidly growing part of the Los Angeles basin,* experienced a substantial increase in NO_2 concentrations. Other California locations and New Jersey

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*From 1965 to 1974, population grew at 4.3% per year in Orange County and only 0.3% per year in Los Angeles County. Traffic levels increased by 7.5% per year in Orange County and only 2.8% per year in Los Angeles County [1].

Table 5.1 Five-Year Changes in Ambient NO_2 Concentrations

STATIONS		NET PERCENTAGE CHANGE IN NO_2 CONCENTRATIONS FROM 1969 TO 1974		
		Annual Mean	90th Percentile	Yearly Maximum
LOS ANGELES BASIN SITES				
Orange County: (rapid growth)	Anaheim	+ 9%	+ 5%	+13%
	La Habra	+99%	+60%	+72%
Average for Orange County		+54%	+33%	+43%
Los Angeles County: (slow growth)	Azusa	+17%	+ 7%	+ 6%
	Lennox	- 7%	-11%	+ 1%
	Los Angeles	+ 3%	- 2%	-31%
	L.A. (Westwood)	+ 8%	+11%	+32%
	L.A. (Reseda)	- 4%	-10%	-13%
Average for Los Angeles County		+ 3%	- 1%	- 1%
OTHER CALIFORNIA SITES				
	Oakland	- 7%	- 9%	-14%
	Pittsburg	- 8%	- 4%	-12%
	Redwood City	-24%	-25%	- 9%
	Salinas	- 1%	- 1%	+27%
	San Rafael	+ 5%	0%	0%
	Santa Cruz	+15%	-24%	-27%
	Stockton	- 3%	-44%	-21%
Average for Other California Sites		- 3%	-15%	- 8%
NEW JERSEY SITES				
	Bayonne	-27%	-18%	-36%
	Camden	- 9%	- 7%	-52%
	Newark	- 5%	0%	+17%
Average for New Jersey Sites		-14%	- 8%	-24%
OTHER SITES				
	Chicago, IL	+32%	+51%	+94%
	Portland, OR	- 4%	+44%	-16%

locations witnessed a moderate improvement in NO_2 air quality. The Chicago site evidently underwent a substantial worsening of NO_2 air quality.

Table 5.2 presents ten-year changes in ambient NO_2 concentrations. Over the ten years, Los Angeles County, Stockton, and Chicago all show significant increases in annual mean NO_2 concentrations. This increase is presumably due to increases in NO_x emissions over the decade. NO_x emissions increased because of traffic growth and because the controls initially used to reduce HC and CO in new cars had the side effect of raising NO_x emissions. A recent study indicates that NO_x emissions increased by about 29% in Los Angeles County from 1964 to 1974 [1]. This is only slightly above the 22% increase in annual mean NO_2 concentrations for the county.

A very interesting feature of Table 5.2 is the trend in 90th percentile and yearly maximum concentrations in Los Angeles County and Stockton, California. In contrast to the increase in annual mean NO_2 concentrations, the 90th percentiles showed little change over the decade, and the yearly maxima showed a moderate decrease. We are not sure why this is the case. The most plausible explanation involves HC controls. California, in particular Los Angeles County, has achieved significant HC control over the decade. The decrease in HC levels may have an amelioratory effect on ambient NO_2 levels, especially maximum NO_2 concentrations. This hypothesis is supported by a study which showed that daily maximum NO_2 concentrations increased less than daily maximum NO_x concentrations in the Los Angeles basin over the past decade [1]. A second explanation involves changes in the spatial

Table 5.2 Ten-Year Changes in Ambient NO_2 Concentrations

STATIONS		NET PERCENTAGE CHANGE IN NO_2 CONCENTRATIONS FROM 1964 TO 1974		
		Annual Mean	90th Percentile	Yearly Maximum
LOS ANGELES BASIN SITES				
Los Angeles County:	Azusa	+66%	+32%	+39%
	Burbank	+28%	+21%	+ 5%
	Lennox	- 9%	-25%	-35%
	Long Beach	+18%	+ 5%	-23%
	Los Angeles	+18%	+ 3%	-20%
	L.A. (Westwood)	+27%	+12%	+31%
	L.A. (Reseda)	+18%	+ 7%	-21%
	Pomona	+ 9%	0%	+ 7%
Average for Los Angeles County		+22%	+ 7%	-17%
OTHER CALIFORNIA SITES				
	Stockton	+45%	- 2%	-17%
NON-CALIFORNIA SITES				
	Chicago, IL	+40%	+60%	+46%

distribution of emissions. On both a local and regional scale, source growth occurs in a spreading fashion. As the spatial distribution of emissions becomes more spread out, maximal concentrations may be reduced relative to mean concentrations. This second hypothesis fails, however, to explain the historical decreases in maximal NO_2 relative to maximal NO_x.

5.2 YEAR-TO-YEAR TRENDS IN NO_2 AIR QUALITY

The previous section presented overall air quality trends for five- and ten-year periods. A given overall trend can occur in a variety of ways, i.e., a variety of year-to-year patterns. The year-to-year pattern in the trend is important in relating air quality changes to source growth and control strategies. This section discusses the year-to-year changes in NO_2 air quality for several regions.

With the original data base that was subject to the 75% completeness criterion, it is difficult to examine year-to-year trends at certain stations because many years of data fail the completeness test. The data base for trend analysis can be expanded considerably by including years with at least 50% complete data, and by interpolating for years with less than 50% complete data. This expanded data base has been assembled for several areas of the country. All the data which have been added have been subjected to the quality control procedures of Chapter 2, and all reported maxima have been adjusted for sample size according to the method described in Chapter 3.

5.2.1 Trends at CAMP Sites

Figure 5.1 presents year-to-year trends averaged over 4 CAMP sites (Denver, Chicago, St. Louis, and Cincinnati) from 1964 to 1973.[*] Yearly values and three-year moving averages are plotted for the annual mean, the 90th percentile, and the annual one-hour maximum. Since the SAROAD printout did not include annual means for several of the years, the 50th and 70th

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[*] Of the 6 CAMP sites, Washington D.C. is not included because of a change in station location, and Philadelphia is excluded because of the lack of data for 1972 and 1973.

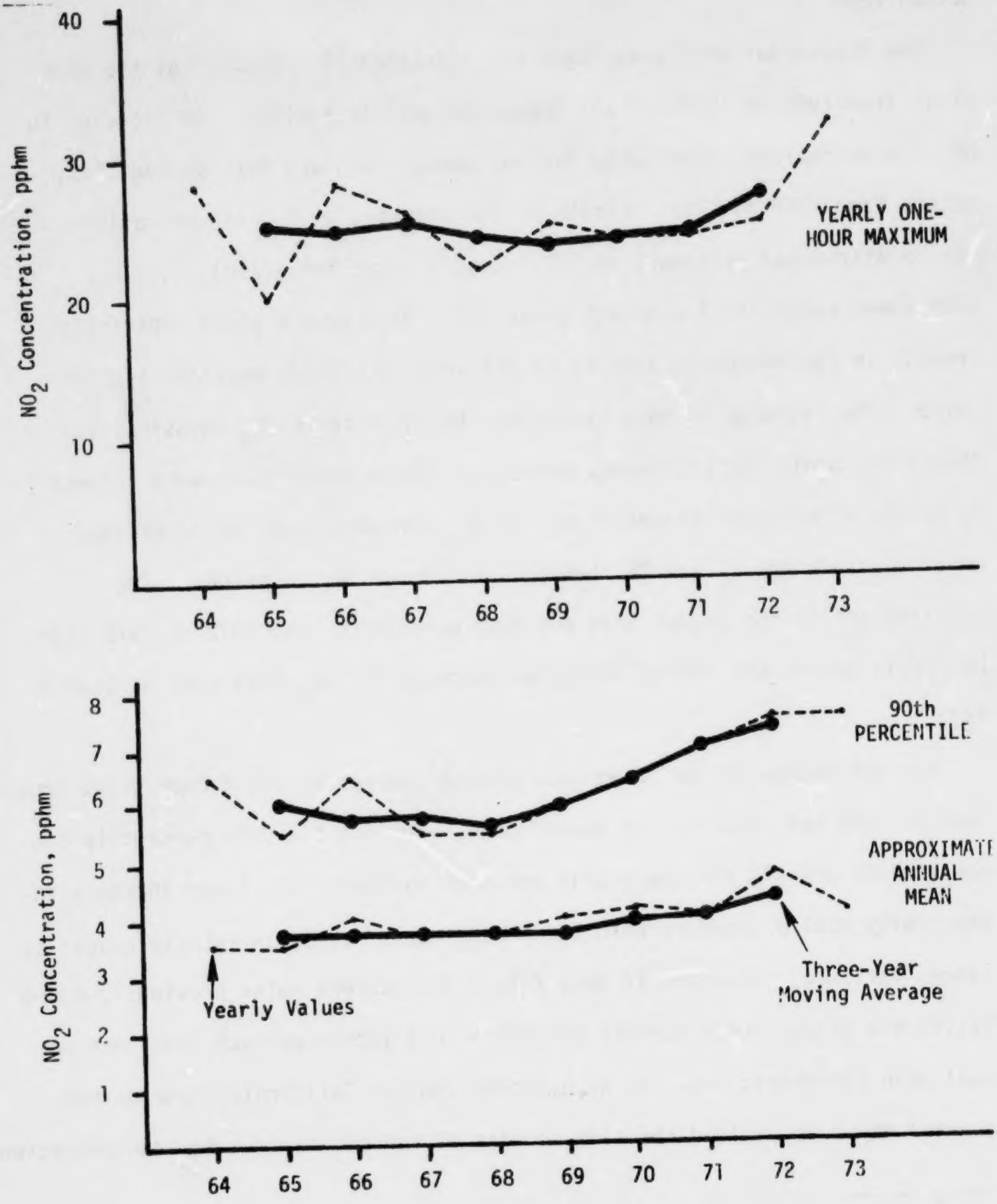

Figure 5.1 NO_2 Air Quality Trends at 4 CAMP Sites (Denver, Chicago, St. Louis, and Cincinnati)

percentiles were averaged each year to provide an estimate of the annual mean.*

The three-year moving averages are approximately constant at the CAMP sites from 1965 to 1968 for all three air quality indices. An increase in NO_2 concentrations, especially for the annual mean and 90th percentiles, occurs from 1968 to 1972. Little of the increase in NO_2 concentrations can be attributed to growth in VMT (vehicle miles travelled). The 4 CAMP urban areas are low-growth areas [2]. Slow growth would especially prevail in the center-city parts of the areas where the monitors are located. The increase is most likely due to the rise in NO_x emissions for 1968-1972 model-year light-duty vehicles. Those model-years were subject to HC and CO emission standards but no NO_x standard, and the technology used to attain the HC and CO standards increased NO_x emissions. The leveling off of the annual mean and 90th percentile from 1972 to 1973 might be partly due to the federal emission standard for NO_x that came on line in 1973.

The net change in the three-year moving average at the 4 CAMP sites from 1965 to 1972 was +16% for the annual mean, +20% for the 90th percentile concentration, and +7% for the yearly one-hour maximum. The lower increase in the yearly maxima compared with the annual means may be an anomaly caused by random variance. However, it does follow the pattern noted previously among California sites, where maximal concentrations increased much less than annual mean concentrations. As we hypothesized for California, hydrocarbon control may have yielded the side benefit of reduced maximal NO_2 concentrations.

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*Overall, the average of 50th and 70th percentiles provided a quite good estimate of the annual mean.

Significant decreases in hydrocarbon (and oxidant) concentrations at CAMP sites have recently been documented [3]. Another explanation for the lesser increase in maximal concentrations could be the spreading-out of emissions (see discussion on pages 92 and 93).

5.2.2 Trends at New Jersey Sites

Figure 5.2 summarizes trends averaged over 2 New Jersey sites (Bayonne and Newark) from 1966 to 1974. In this case, there was a slight improvement for all three air quality indices. Three-year averages decreased 12% for the annual mean, 9% for the 90th percentile, and 13% for the yearly maximum from 1967 to 1973.

For the two New Jersey sites, the increase in automotive emissions from 1968 to 1972 is not apparent in the air quality trends. We are not sure why. Possibly, reductions in stationary area source NO_x emissions, caused by conversions to natural gas, may have compensated for the increase in vehicular emission factors. It is also noteworthy that northern New Jersey is a low-growth area; there may have actually been negative growth in the environs of the monitor. A striking feature of the trends is the decrease in NO_2 concentrations from 1973 to 1974. This may be largely due to the energy crisis and the associated reduction in VMT that occurred in 1974.

As with California sites and CAMP sites, yearly maximal NO_2 levels decreased by more than annual mean levels in New Jersey. However, the difference in the trends (-13% vs. -12%) is certainly not statistically significant.

5.2.3 Trends in Coastal/Central Los Angeles County

Los Angeles County provides high-quality aerometric and emission data that are very suitable for trend analyses. The coastal/central areas of

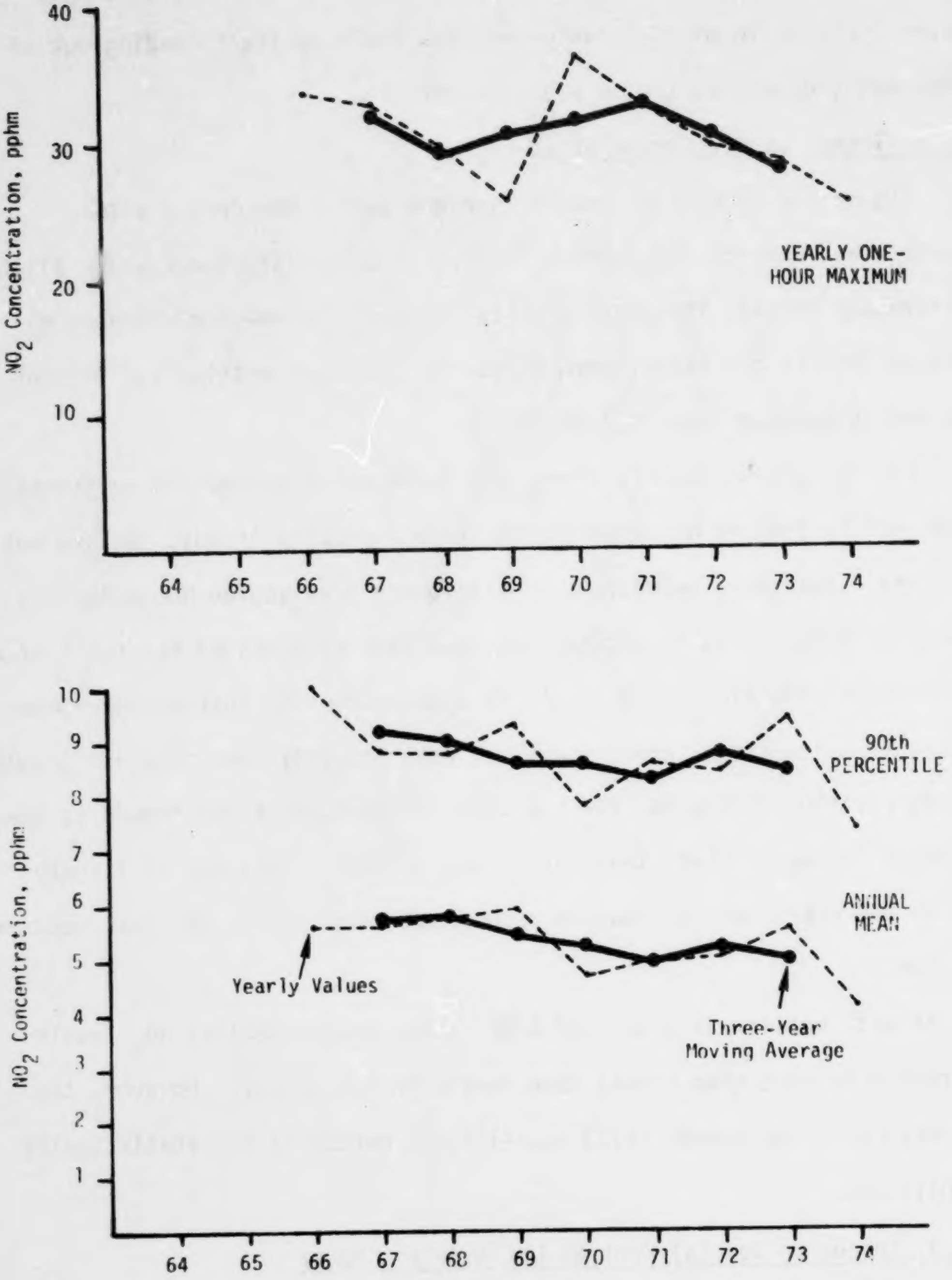

Figure 5.2 NO_2 Air Quality Trends at 2 New Jersey Sites (Bayonne and Newark)

Los Angeles County are particularly interesting because of the reductions in hydrocarbons that have been achieved in those areas. Figure 5.3 summarizes NO_2 air quality trends at 6 coastal/central stations in Los Angeles County from 1964 to 1974.*

For all three air quality indices, three-year moving averages of NO_2 concentrations increased slightly from 1965 to 1970 and decreased from 1970 to 1973. This reflects changes in automotive-emission factors. NO_x emissions increased substantially in 1966 to 1970 model-year vehicles due to the "leaning out" of engines for HC and CO control. California established emission standards for NO_x starting in 1971. Growth in traffic has not had great effect on trends in this part of the Los Angeles basin. VMT grew at 2.8% per year in Los Angeles County from 1965 to 1974 [1]. However, most of the VMT growth occurred in portions of the county away from the older, well-established, central business districts where the 6 monitors in question are located.

The net changes in three-year moving averages of NO_2 concentrations from 1965 to 1973 are +13% for the annual mean, +2% for the 90th percentile, and -8% for the yearly one-hour maximum. The increase in the annual mean NO_2 concentrations is slightly less than the increase in mean NO_x concentrations at these 6 stations (approximately +20%) [4]. Increases in 90th percentile NO_2 concentrations and yearly maximum NO_2 concentrations are even less than the increase in annual mean NO_2 levels. The varied trends may be due to hydrocarbon control. It is possible that hydrocarbon control has

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*These stations are Burbank, Lennox, Long Beach, Downtown Los Angeles, Westwood, and Reseda.

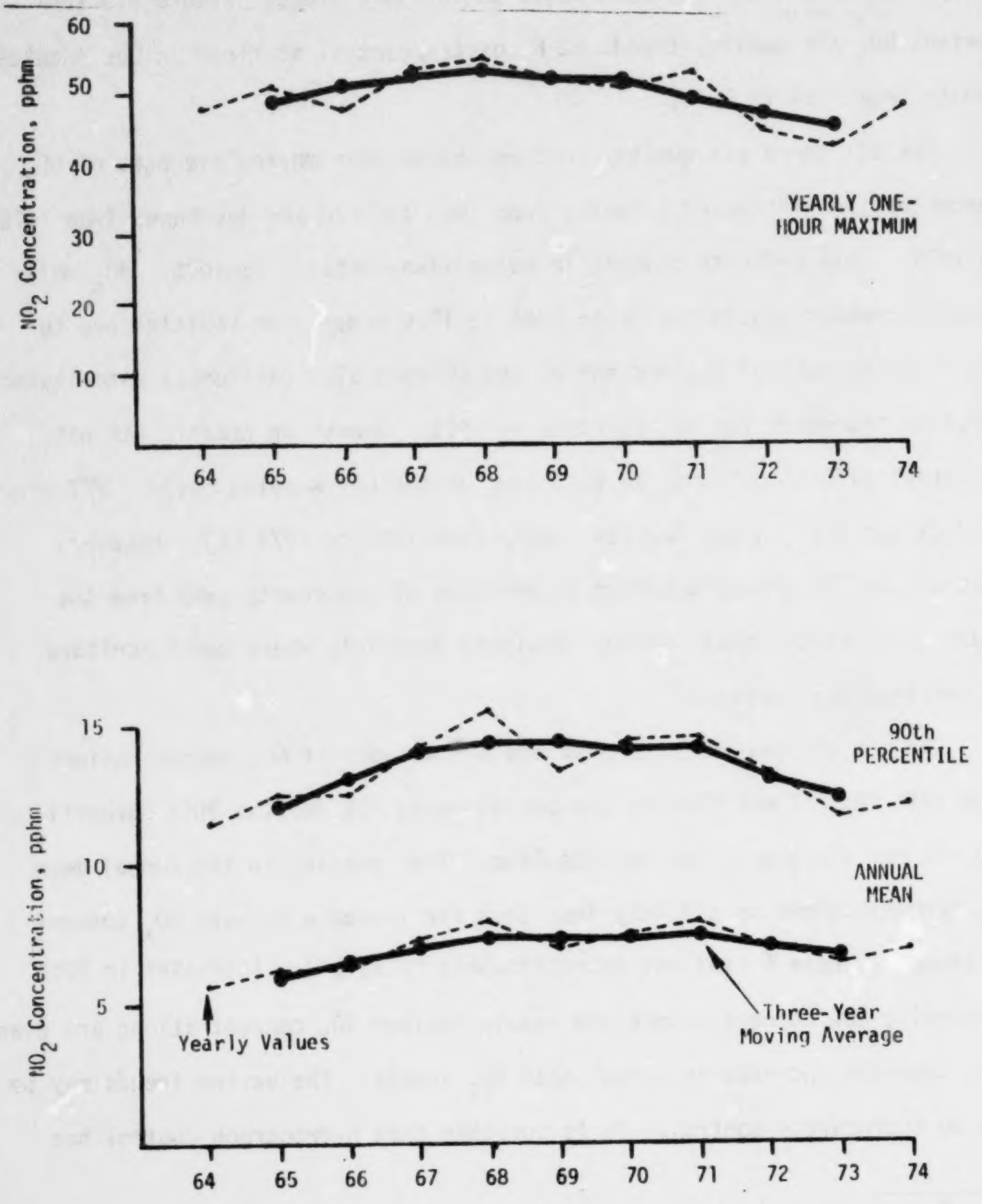

Figure 5.3 NO_2 Air Quality Trends at 6 Sites in Coastal/Central Los Angeles County

slightly reduced annual mean NO_2 levels relative to annual mean NO_x levels. Even more plausible is the contention that HC reductions have yielded significant benefits with respect to maximal NO_2 concentrations. Part II of this report, which involves empirical models of the NO_2/precursor relationship, should shed more light on these issues. Models are developed for both annual mean and yearly maximum NO_2 concentrations.

5.3 REFERENCES

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2. U.S. Bureau of the Census, *Statistical Abstract of the United States: 1975*, Washington, D.C., 1975.

3. A.P. Altshuller, "Evaluation of Oxidant Results at CAMP Sites in the United States," *Journal of the Air Pollution Control Association*, Vol. 25, p. 19, 1975.

4. California Air Resources Board, *Ten-Year Summary of California Air Quality Data: 1963-1972*, Sacramento, January 1974.

6.0 RELATIONSHIP OF YEARLY ONE-HOUR MAXIMA AND ANNUAL MEANS

If the existing long-term air quality standard for NO_2 (5 pphm-annual mean) is supplemented with a one-hour standard, it will be important to know when and where each of the standards is the binding constraint for control strategy formulation. Under certain conditions, one of the standards may be obviously binding; under other conditions, both standards may have to be considered. Since a specific one-hour standard has not yet been chosen, we cannot completely solve the problem of determining the binding constraint. Rather, this chapter will provide the information that is required to address the problem once a standard has been set. The required information is based on an analysis of spatial and temporal patterns in the ratio of one-hour maximum to annual mean.

A similar problem (determining the binding constraint) will arise if a short-term air quality standard is set for 90th percentile concentrations. The information needed to solve that problem can be assembled in a manner entirely parallel to the present analysis. The key variable would then be the ratio of the 90th percentile concentration to the annual mean concentration.

6.1 NATIONWIDE PATTERNS IN THE MAXIMUM/MEAN RATIO

The data base described in Chapter 4 and Appendix C provides information on present ratios of maximum-to-mean NO_2 concentrations. That data base includes yearly one-hour maxima and annual means, averaged from 1972 to 1974, for 120 urban stations and 3 rural/power plant stations. The distribution of maximum/mean ratios for the 120 urban stations is shown in Figure 6.1.

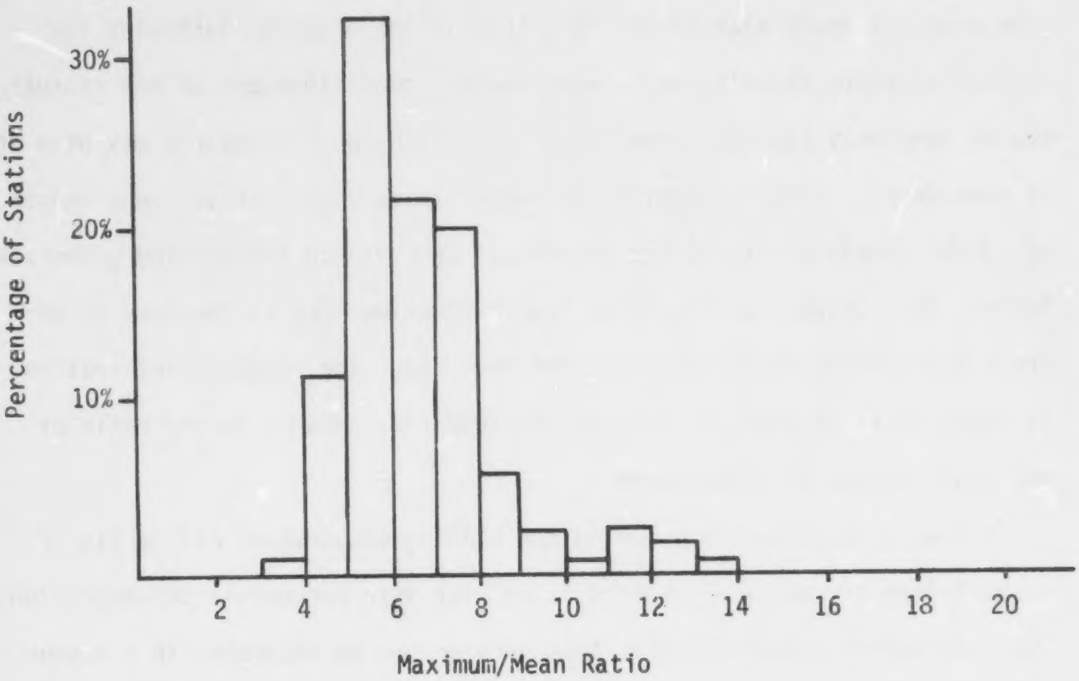

Figure 6.1 Distribution of Maximum/Mean NO_2 Ratios for Urban Locations

Figure 6.1 illustrates that the preponderance of urban monitoring sites (85% of the total) have maximum to mean ratios in the range of 4 to 8. One of the 120 stations, Syracuse (011), New York, has a ratio of 3.8, slightly less than 4. Seventeen of the urban stations, 14% of the total, have ratios of 8 or greater. Table 6.1 lists these stations.

There does not appear to be any general geographical pattern in Table 6.1. Seven of the seventeen sites are in California, but this is not unusual because half of the 120 urban monitoring sites are in California.

Table 6.1 Locations with Maximum/Mean Ratios Exceeding 8, 1972-1974

Station	Maximum/Mean Ratio	Station	Maximum/Mean Ratio
Ojai, CA	13.4	Glen Falls, NY	9.0
Phoenix, AZ	12.2	Silver Spring, MD	8.8
Barstow, CA	12.0	Reno, NV	8.5
St. Louis (006), MO	11.5	Las Vegas, NV	8.4
Chino, CA	11.1	Baltimore, MD	8.1
Ashland, KY	11.0	Los Angeles, (Westwood), CA	8.1
Costa Mesa, CA	10.2	San Jose, CA	8.0
San Diego, CA	9.6	Redwood City, CA	8.0
Denver, CO	9.2		

Figure 6.1 provides some clues as to whether a one-hour or annual mean standard would be the binding constraint. If a federal one-hour standard were established at the level of the California one-hour standard (25 pphm), and if the maximum and mean responded equivalently to emission control,

then a maximum/mean ratio of 5 would be the dividing point for a binding one-hour standard vs. a binding annual mean standard. Figure 6.1 indicates that the one-hour standard would be binding for 88% of the urban locations. If a federal one-hour standard were set at 50 pphm, and if the maximum and mean responded equivalently to emission changes, then the critical maximum/mean ratio would be 10. For this case, the present annual mean standard would be the binding constraint for 94% of the locations. Before too much is read into this simplistic analysis, we should note that the assumption of the maximum and mean responding equivalently to emission control seems to be a poor one. As noted earlier, the maximum-to-mean NO_2 ratio evidently changes with time. In Part II we will find evidence that this occurs because HC control reduces maximal NO_2 levels preferentially over mean NO_2 levels. If emission control can significantly alter the maximum/mean ratio, then it may be best to consider both the annual mean and one-hour standard for every location in formulating strategies for attainment and maintenance of the NAAQS.

Figure 6.2 illustrates the national geographic pattern of maximum/mean NO_2 ratios. To avoid cluttering the map, not all of the 120 urban stations are included. Where there are several stations in close proximity, the stations with the highest and lowest ratios are recorded on the map to illustrate the range in the ratio. Figure 6.2 reveals no broad nationwide patterns in the maximum/mean NO_2 ratio. Both the western and eastern sites show about the same maximum/mean ratio, typically ranging from 5

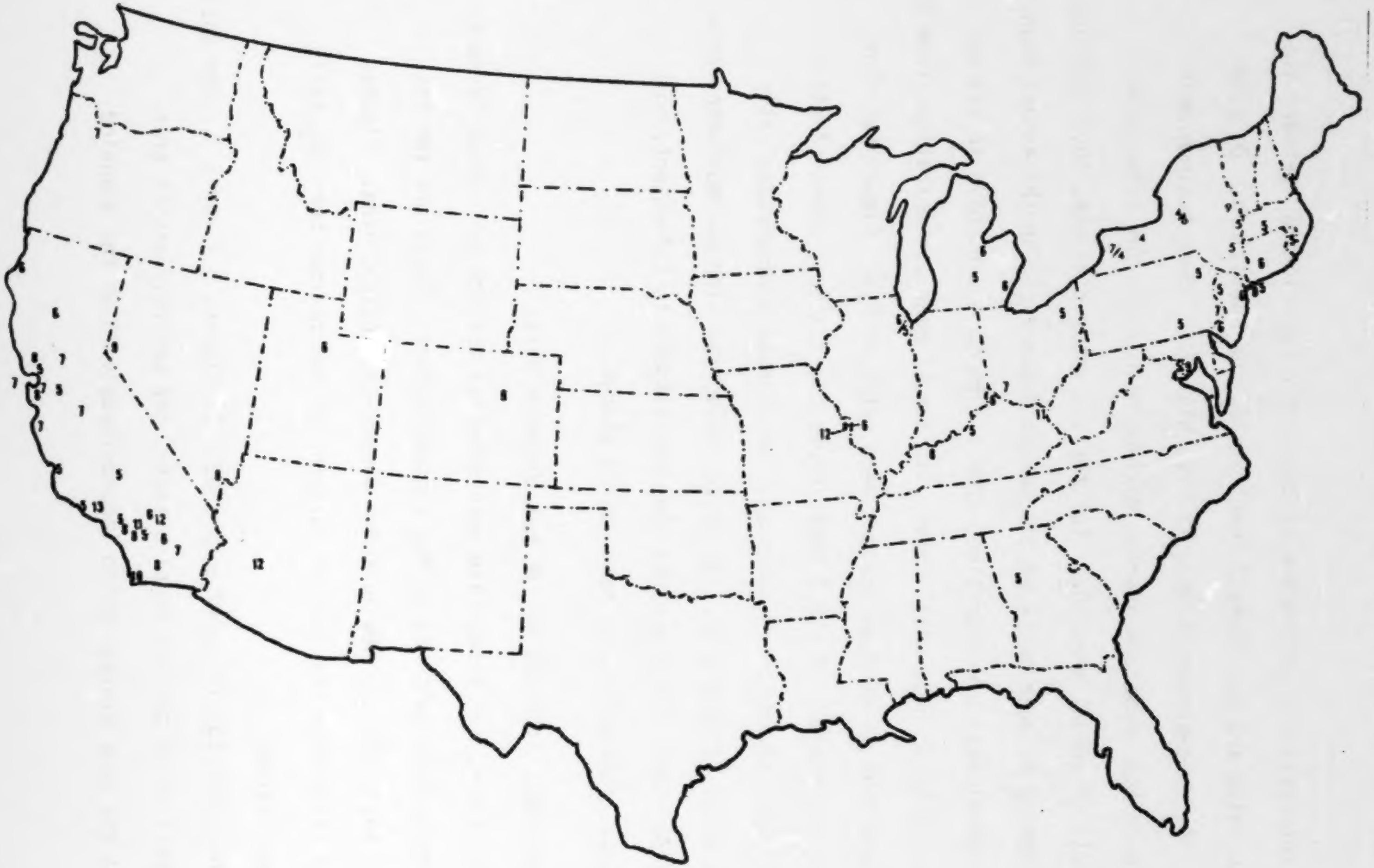

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Figure 6.2 Nationwide Geographic Distribution of Maximum/Mean NO_2 Ratio at Urban Sites, 1972-1974

to 12; also, no discernable gradient in the ratio is apparent from north to south.

It is interesting to determine if there is a relationship between the maximum/mean ratio and the overall level of NO_2 concentrations. Do sites with higher NO_2 concentrations tend to have higher or lower maximum/mean ratios? Figure 6.3 shows the average maximum/mean ratio for sites with various levels of annual mean NO_2. For the 120 urban stations, there appears to be essentially no dependence of the maximum/mean ratio on the annual mean. Sites with annual mean concentrations from 1 pphm to 4 pphm have an average maximum/mean ratio of 6.5, while sites with annual mean concentrations from 4 pphm to 8 pphm have an average maximum/mean ratio of 6.4. Figure 6.3 also demonstrates the anomaly of the 3 rural/power plant sites. These 3 sites have annual means of about 0.8 pphm, and the average maximum/mean ratio among these sites is nearly 20. As noted above, the high maximum/mean ratio is expected for these sites because they are subject to infrequent, but rather intense, fumigations by power-plant plumes.

6.2 INTRAREGIONAL PATTERNS IN THE MAXIMUM/MEAN RATIO

In this study, two areas have been selected for the purpose of investigating intraregional patterns in NO_2 concentrations. These are the Los Angeles air basin and the New York-New Jersey-New England area. Figures 6.4 and 6.5 illustrate the spatial patterns of the maximum/mean NO_2 ratio within these regions.

No consistent spatial gradients appear in Figures 6.4 and 6.5. The most populated portion of the Los Angeles basin, the central/coastal area, shows about the same average ratio (approximately 7) as the downwind

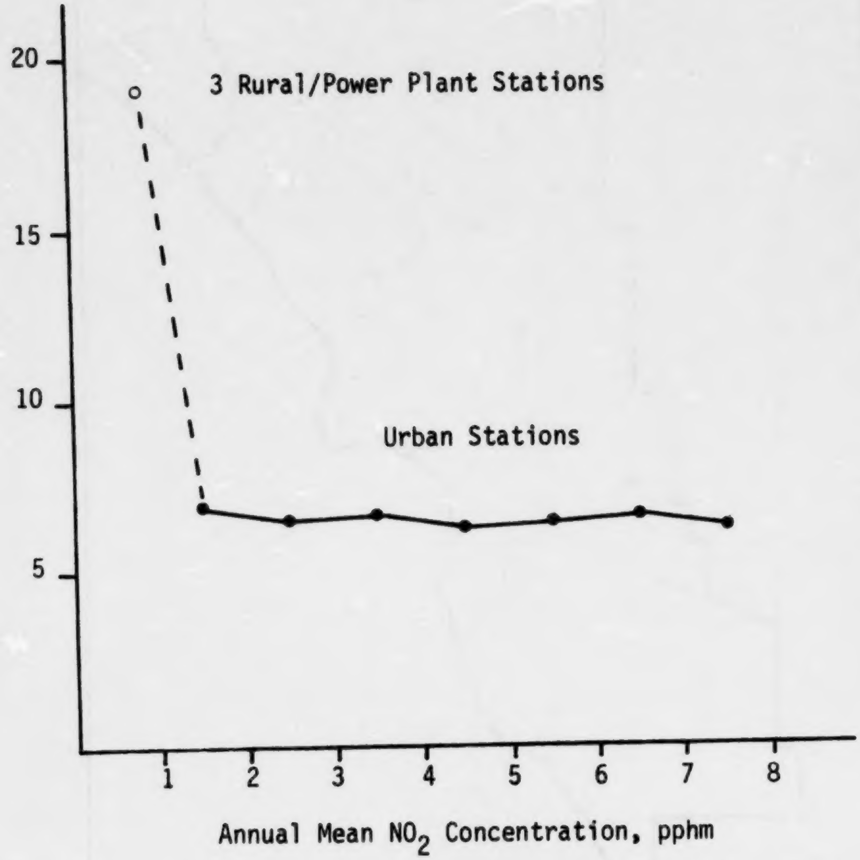

Figure 6.3 Dependence of Maximum/Mean Ratio on Annual Mean NO_2 Concentrations

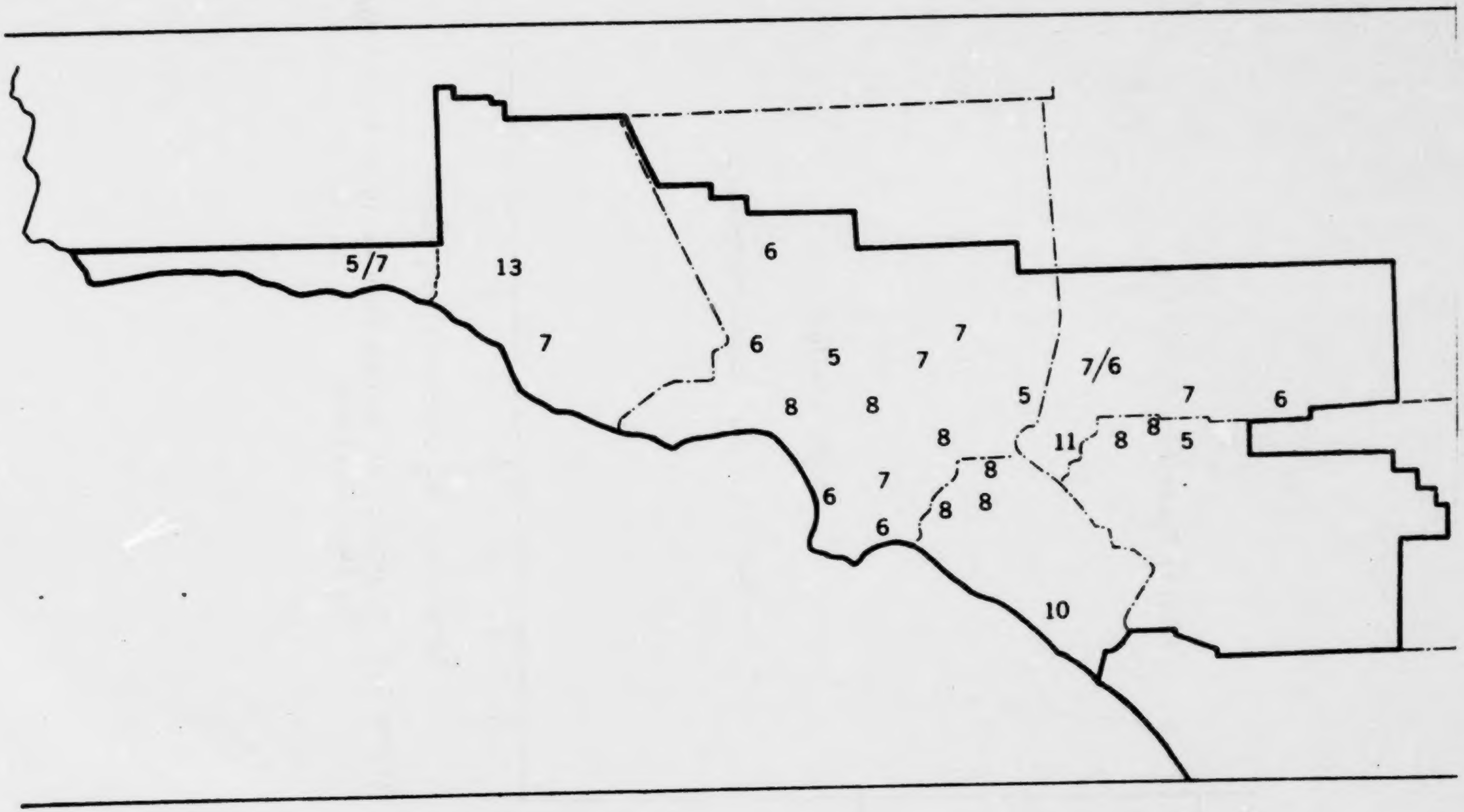
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Figure 6.4 Maximum/Mean NO_2 Ratio at Monitoring Sites in the Los Angeles Region, 1972-1974

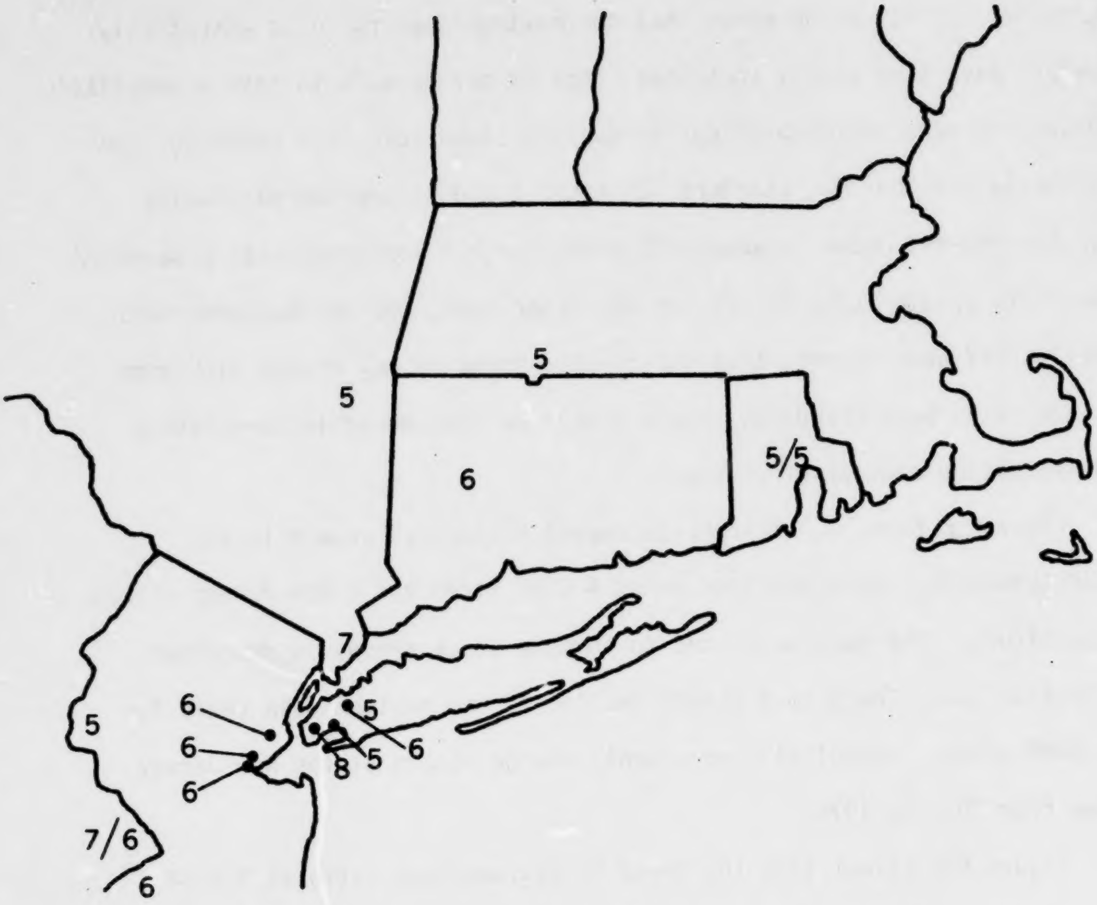
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Figure 6.5 Maximum/Mean NO_2 Ratio at Monitoring Sites in the New York-New Jersey-New England Area, 1972-1974

eastern/inland areas and the isolated northwestern counties (Santa Barbara and Ventura). New York City has about the same ratio (approximately 6) as Philadelphia, northern New Jersey, New Britain, CT, Springfield MA, and Providence, RI.

6.3 HISTORICAL TRENDS IN THE MAXIMUM/MEAN RATIO

It is important to investigate historical trends in the maximum/mean NO_2 ratio. If it can be shown that the maximum/mean ratio is essentially constant over time at all locations, then it may be safe to take a simplistic approach in determining binding air quality standards. For instance, the California one-hour NO_2 standard (25 pphm) could be considered binding over the federal annual standard (5 pphm) for all locations with a maximum/mean ratio greater than 5. If, on the other hand, the maximum/mean ratio shows significant trends, then the binding standard may change with time. In this case, both standards should always be considered in formulating and evaluating control strategies.

Figures 6.6 and 6.7 illustrate recent historical trends in the maximum/mean NO_2 ratio averaged among 4 CAMP sites and 2 New Jersey sites, respectively. The data base used to compute these trends is described in Section 5.2. There is a slight decline in the maximum/mean ratio for the CAMP sites. Essentially no overall change occurs at the New Jersey sites from 1966 to 1974.

Figure 6.8 illustrates the trend in maximum/mean ratio at 6 sites in the central/coastal part of Los Angeles County. A persistent decline in the ratio is evident; the three-year moving average decreases by 19% from 1965 to 1973. As previously discussed, a possible explanation for

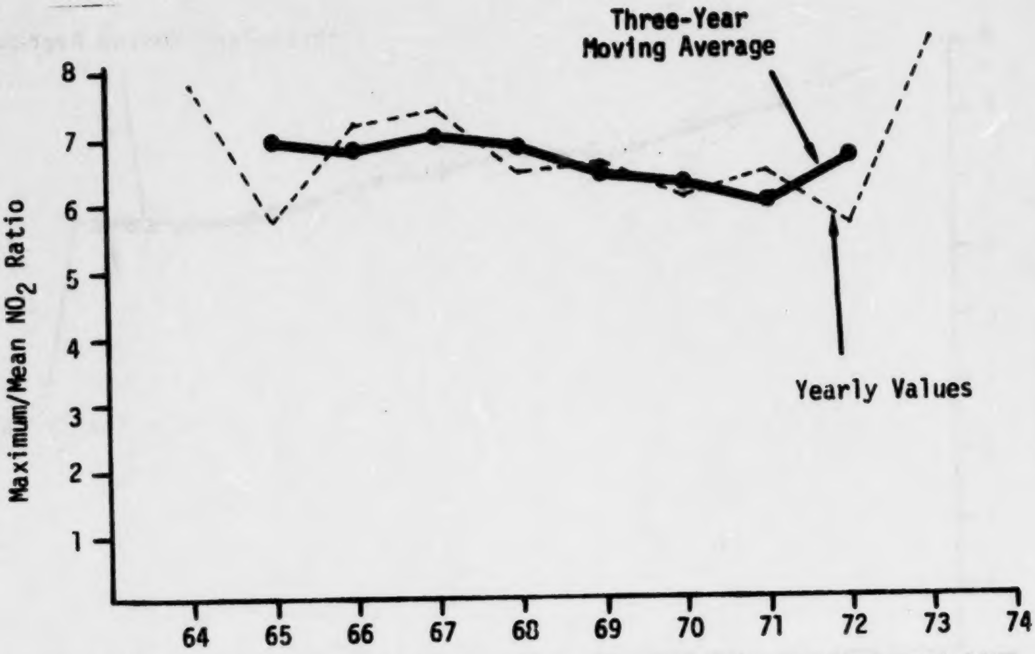

Figure 6.6 · Trends in the Maximum/Mean NO_2 Ratio Averaged over 4 CAMP Sites (Denver, Chicago, St. Louis, and Cincinnati)

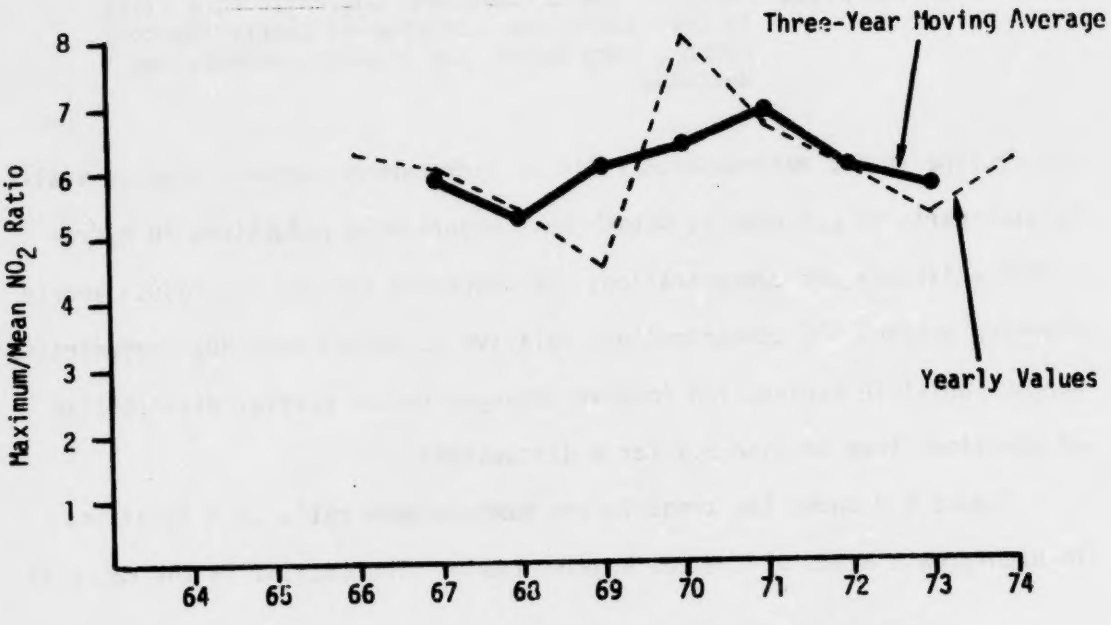

Figure 6.7 Trends in the Maximum/Mean NO_2 Ratio Averaged over 2 New Jersey Sites (Bayonne and Newark)

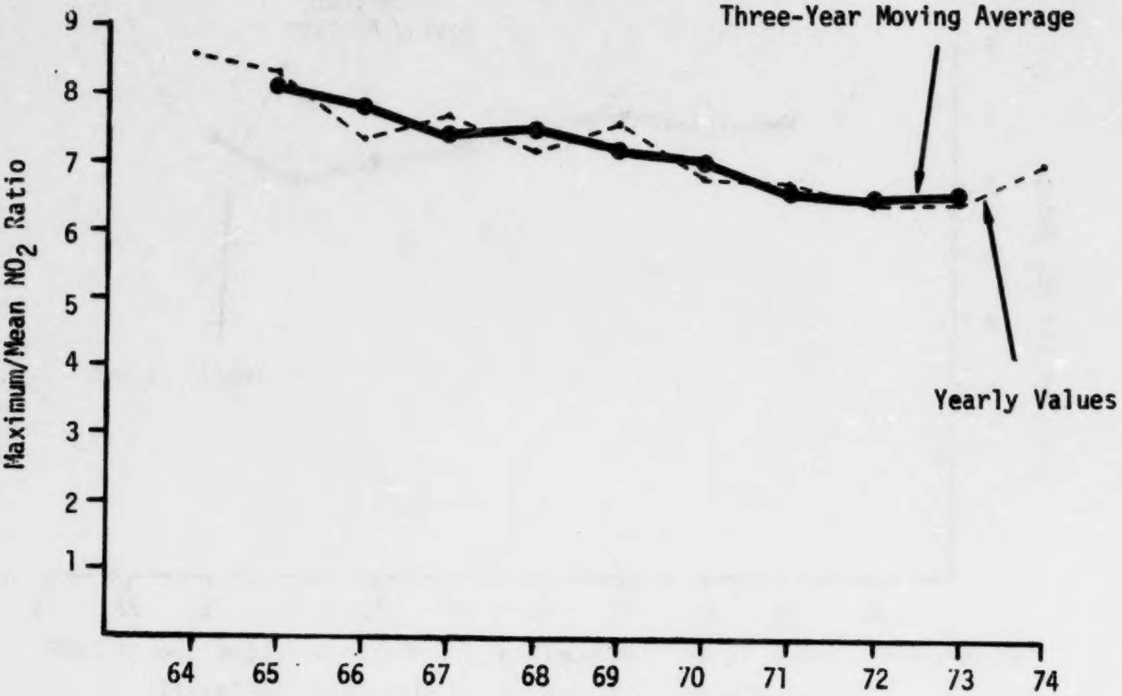

Figure 6.8 Trends in the Maximum/Mean NO_2 Ratio at 6 Sites in Coastal/Central Los Angeles County (Burbank, Lennox, Long Beach, Los Angeles, Reseda, and Westwood)

the decline in the maximum/mean ratio is hydrocarbon control. The central/coastal parts of Los Angeles County have experienced reductions in hydrocarbon emissions and concentrations. Hydrocarbon control may reduce yearly one-hour maximal NO_2 concentrations relative to annual mean NO_2 concentrations. Another possible explanation involves changes in the spatial distribution of emissions (see Section 5.1 for a discussion).

Figure 6.9 shows the trend in the maximum/mean ratio at 5 locations in high-growth areas of the Los Angeles basin. The decline in the ratio is

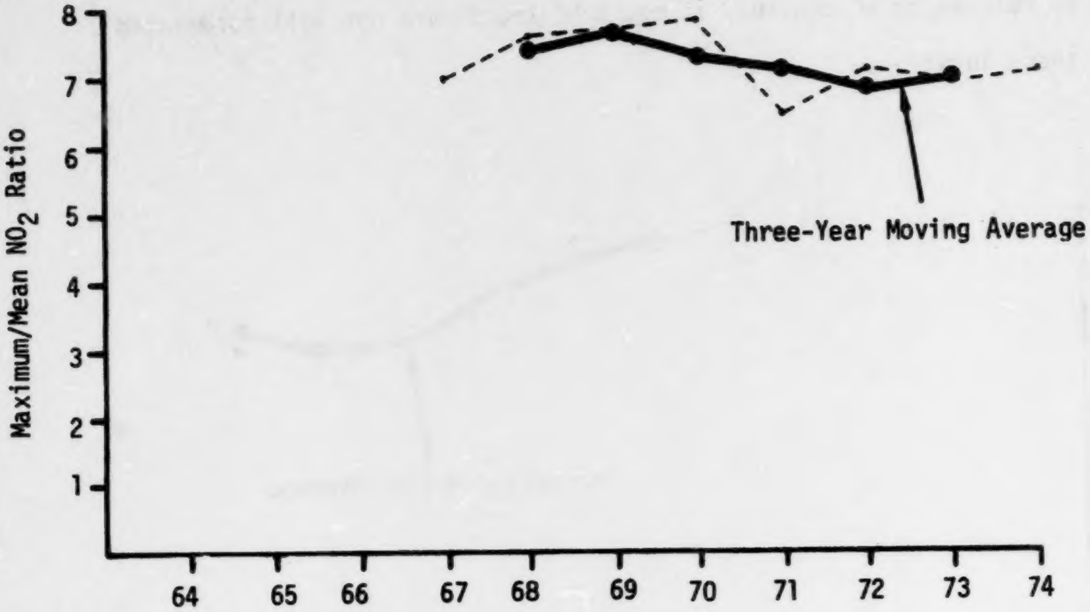

Figure 6.9 Trends in the Maximum/Mean NO_2 Ratio at 5 High-Growth Locations within the Los Angeles Basin (Anaheim, La Habra, Azusa, Pomona, San Bernardino)

now very slight; the three-year moving average decreases only 5% from 1968 to 1974. The high-growth areas of the Los Angeles basin have experienced little reduction in HC emissions. Emission controls in these areas have been counterbalanced by increases in traffic and in the number of other sources. The slower rate of decline in Figure 6.9 relative to Figure 6.8 is consistent with the hypothesis that HC control is a significant factor in reducing maximal NO_2 concentrations.

Figure 6.10 illustrates trends in the maximum/mean ratio at 5 locations in central California. The ratio shows a substantial rate of decline; the three-year moving average decreases by 17% from 1968 to 1973. Again, this may be related to HC control, although HC trends are not well documented for these locations.

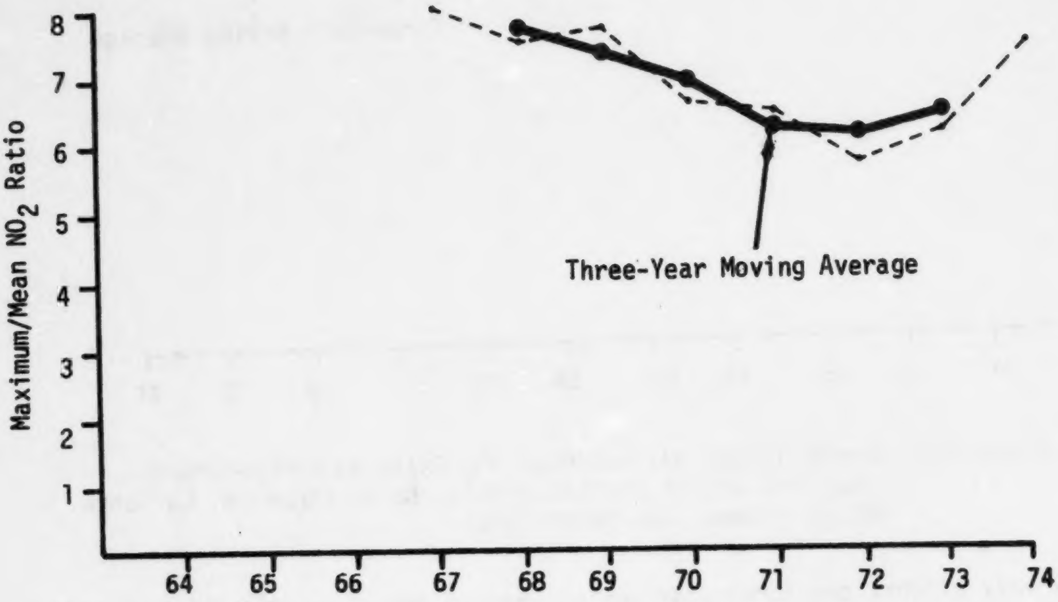

Figure 6.10 Trends in Maximum/Mean NO_2 Ratio at 5 Locations in Central California (Redwood City, Salinas, San Rafael, Santa Cruz, Stockton)

PART II:

EMPIRICAL MODELS OF THE NO_2/PRECURSOR RELATIONSHIP

7.0 EMPIRICAL ANALYSIS OF THE NO_2/PRECURSOR DEPENDENCE

Determining the impact of control strategies or new emission sources on air quality requires a method of translating emission changes into air quality changes. The conventional method for nitrogen dioxide is to model total NO_x as an inert primary pollutant and to assume that NO_2 concentrations are directly proportional to ambient NO_x concentrations, with the proportionality constant equated to the existing atmospheric ratio of NO_2 to NO_x. This approach has some merit, because it is generally agreed that ambient NO_2 levels should be approximately proportional to ambient NO_x levels, with all other factors held constant. However, other factors are not always invariant. In particular, hydrocarbon emission reductions may affect ambient NO_2 concentrations. If we are to predict changes in NO_2 air quality with more confidence, we must know the dependencies of NO_2 concentrations on both photochemical precursors, hydrocarbons as well as NO_x.

Experimental studies with smog chambers have provided most of our present understanding of the NO_2/precursor dependence. The various chamber studies agree on some aspects of the NO_2/precursor dependence, but they disagree on other aspects. Because of these disagreements and because of uncertainty in extrapolating experimental studies to the real atmosphere, there is a need for empirical models that extract information about the NO_2/precursor dependence from ambient data. The purpose of Part II of this report is to develop and apply such empirical models.

This chapter serves as an introduction to Part II. Section 7.1 reviews the results of various experimental studies and summarizes existing knowledge of the NO_2/precursor dependence. Section 7.2 presents the conceptual framework for empirical models. The remaining chapters develop empirical models for various cities and check these models against historical trends and smog-chamber results. Models for both annual mean NO_2 and yearly one-hour maximum NO_2 are included.

7.1 EXPERIMENTAL EVIDENCE OF THE NO_2/PRECURSOR DEPENDENCE

Several researchers have used experimental test chambers (smog chambers) to investigate the dependence of nitrogen dioxide concentrations on the levels of precursor inputs. These experimental studies have provided most of the present understanding of the NO_2/precursor dependence. Before we formulate and apply empirical methods for determining the NO_2/precursor dependence, it is useful to review the results of the smog-chamber experiments. Because both the empirical approach and the smog-chamber approach involve significant uncertainties, it will be important, in the end, to compare the results of both approaches.

Our review of experimental studies will consider results from five smog chamber projects:

- The University of North Carolina (UNC) study using an 11,000-cubic-foot outdoor Teflon chamber, a simulated urban hydrocarbon mix, and twelve-hour irradiations[1];
- The Bureau of Mines study, using a 100-cubic-foot aluminum-glass chamber, auto-exhaust hydrocarbons, and six-hour irradiations[2,3];
- The General Motors study, using a 300-cubic-foot stainless steel-glass chamber, a simulated Los Angeles hydrocarbon mix, and six-hour irradiations[4];

- The HEW study using a 335-cubic-foot chamber, auto-exhaust hydrocarbons, and up to ten-hour irradiation time[5]; and
- The HEW study using a 335-cubic-foot chamber, toluene and m-xylene, and six-hour irradiations[6].

7.1.1 Average NO_2 Concentrations

The various smog-chamber studies apparently yield consistent results concerning the dependence of average NO_2 yield (or NO_2 dosage) on NO_x input. With other factors held constant, average NO_2 concentrations tend to be directly proportional to initial NO_x. The proportional relationship for average NO_2 is illustrated in Figures 7.1 through 7.5.

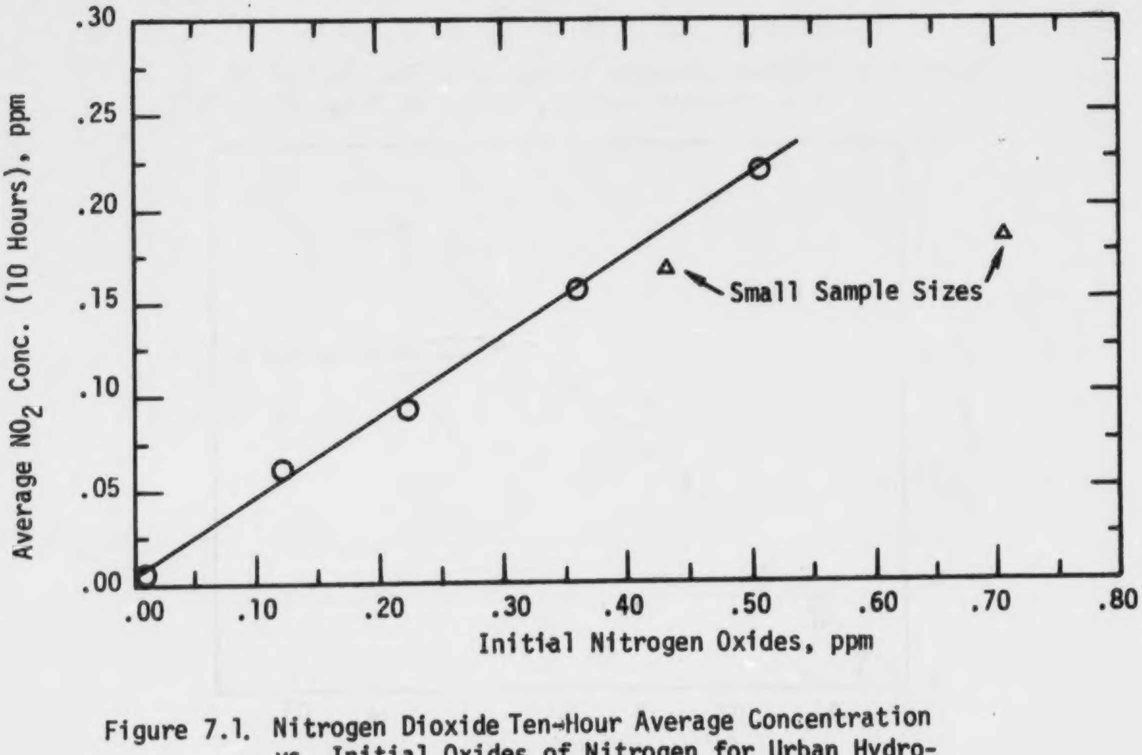

Figure 7.1. Nitrogen Dioxide Ten-Hour Average Concentration vs. Initial Oxides of Nitrogen for Urban Hydrocarbon Mix (Means of Several Experiments), University of North Carolina Study[1]

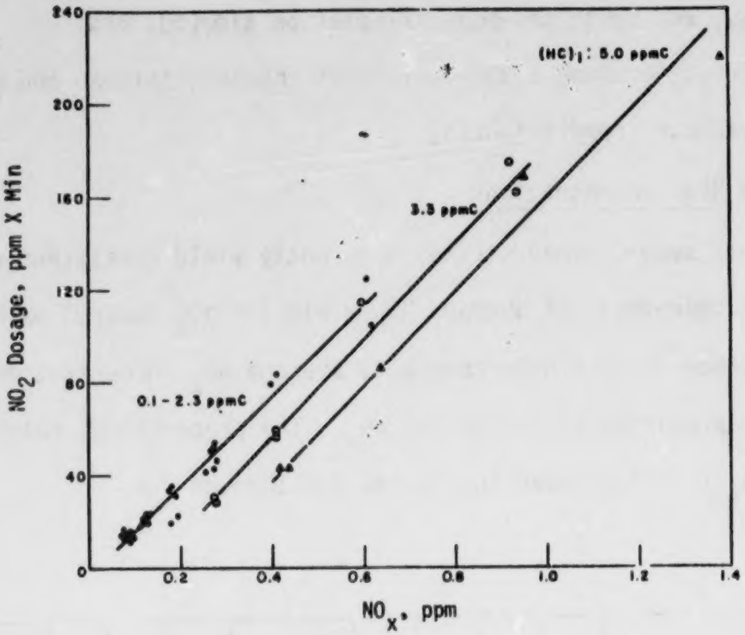

Figure 7.2 Nitrogen Dioxide Dosage as a Function of NO_x at Various HC Levels, Bureau of Mines Study [2]

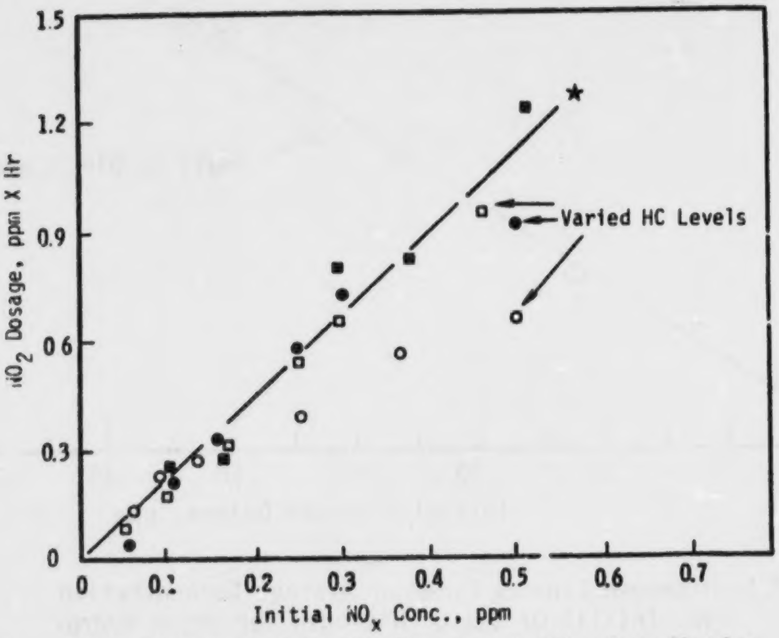

Figure 7.3 Nitrogen Dioxide Dosages in the Irradiation of Multicomponent Hydrocarbon/NO_x Mixtures, General Motors Study [4]

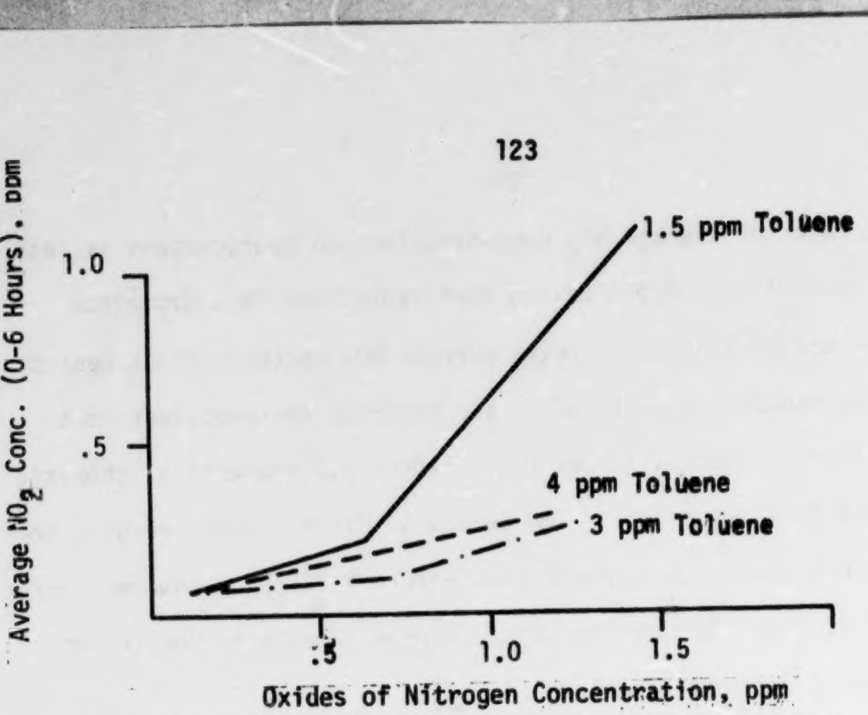

Figure 7.4 Average NO$_2$ Concentration (Over Six Hours) vs. Initial NO$_x$ at Three HC Levels, HEW Study[6]

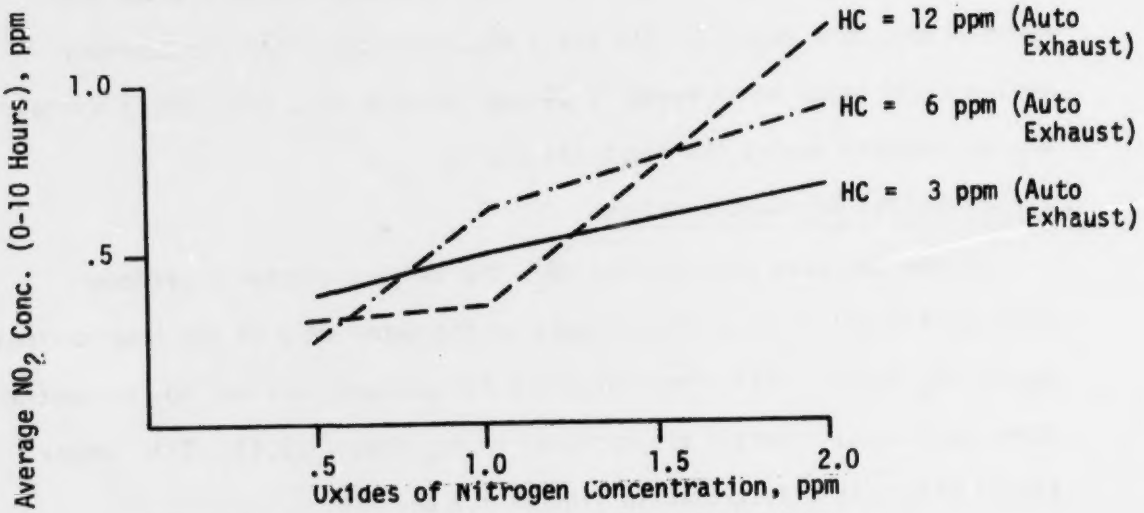

Figure 7.5 Average NO$_2$ Concentration (During First Ten Hours) vs. Initial NO$_x$ at Three HC Levels, HEW Study[5]

The dependence of average NO_2 concentrations on hydrocarbons is less understood. Stephens has hypothesized that reductions in hydrocarbon concentrations should tend to increase average NO_2 concentrations because the hydrocarbon reductions would delay and suppress the reactions that consume NO_2 after it reaches a peak [7]. Figure 7.6 presents a schematic illustration of this hypothesis. The Bureau of Mines chamber results are consistent with Stephens' hypothesis (see Figure 7.2) [2]. However, three other chamber studies indicate that hydrocarbons produce no consistent effect on average NO_2 concentrations [4,5,6].

In direct contradiction to Stephens' hypothesis, the UNC outdoor chamber experiments found that a 50% reduction in hydrocarbons produced about a 20% decrease in average NO_2 [1]. However, in defense of the hypothesis, it should be noted that the UNC chamber runs were of ten-hour duration and that the NO_2 levels at the end of the experiments were greater when hydrocarbons were reduced. The extra NO_2 remaining after the ten-hour period could cause an increase in 24-hour average NO_2, even though average NO_2 was reduced during the first ten hours.

7.1.2 Maximal NO_2 Concentrations

As was the case with average NO_2, the various chamber experiments yield consistent results with respect to the dependence of one-hour maximal NO_2 on NO_x input. With other factors held constant, maximal NO_2 concentrations tend to be directly proportional to NO_x input[1,3,4]. This proportional effect is illustrated in Figures 7.7 and 7.8.

There is less agreement with respect to the dependence of maximal NO_2 concentrations on hydrocarbon input. The Bureau of Mines study

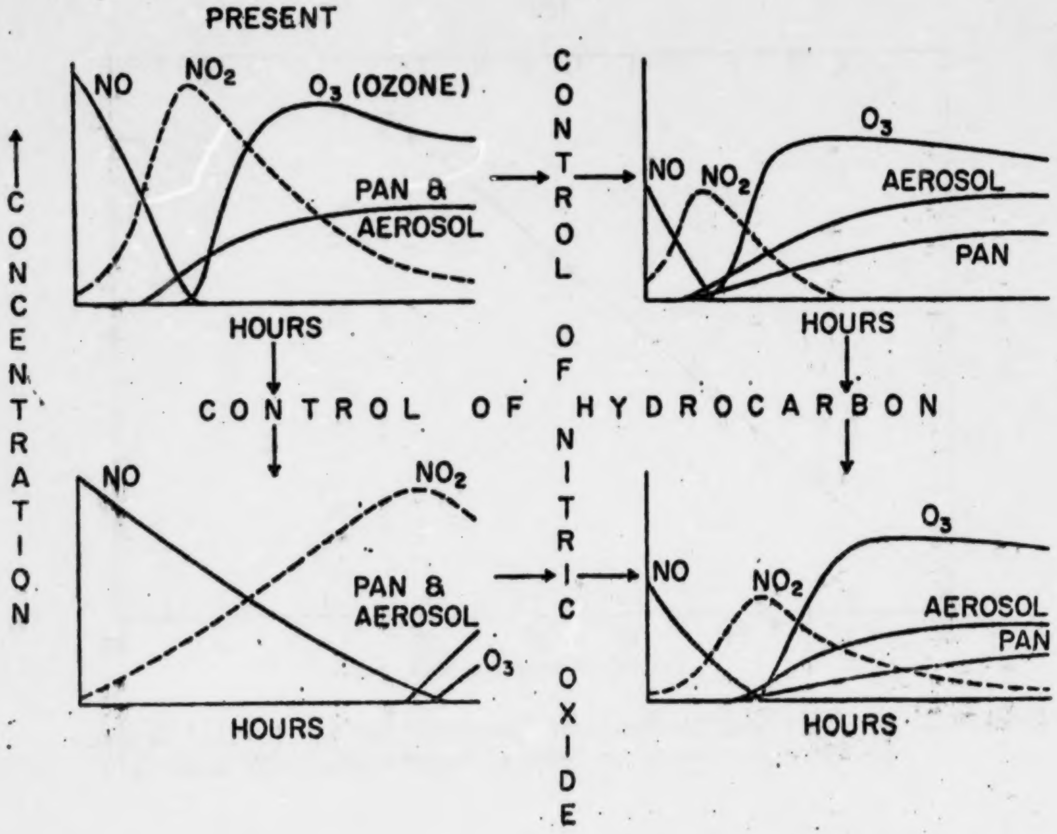

Figure 7.6. Stephens' Hypothesis of Effect of HC and NO_x Control[7]

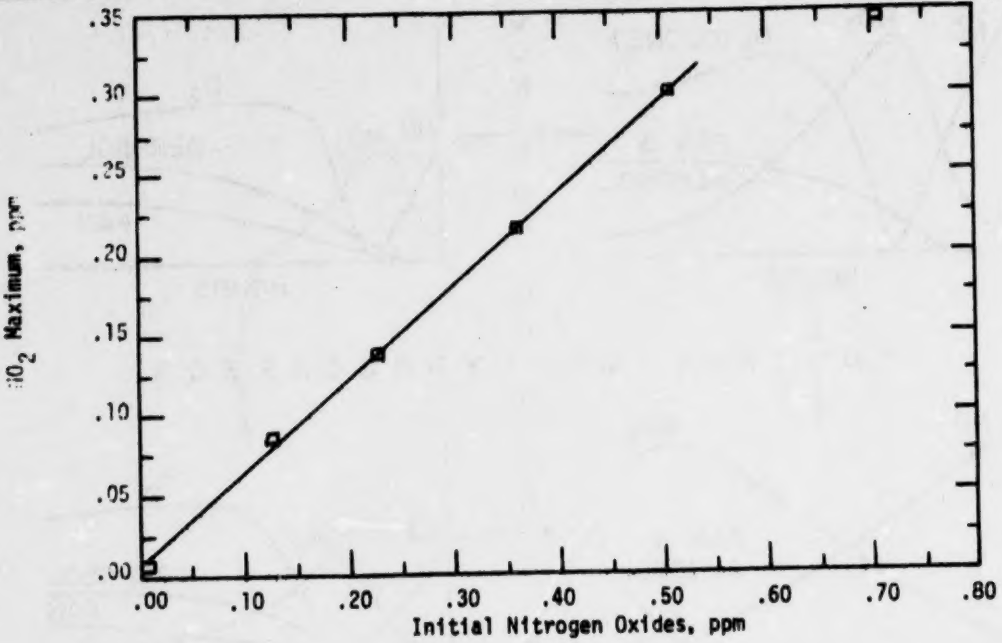

Figure 7.7 Nitrogen Dioxide Maximum Concentration vs. Initial Oxides of Nitrogen (Means of Several Experiments) UNC Study [1]

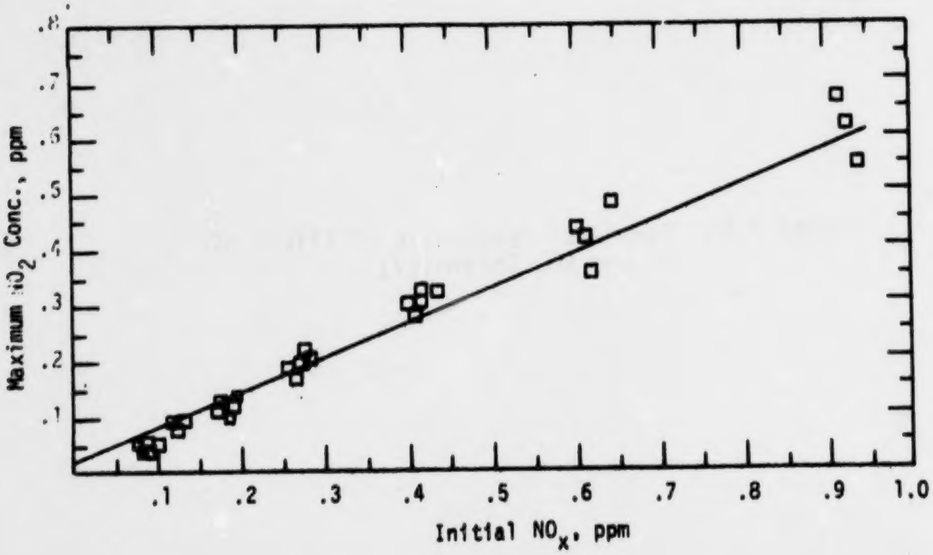

Figure 7.8 Dependence of Nitrogen Dioxide Maximum Concentration on Initial Nitrogen Oxides, Bureau of Mines Study [3]

found that maximal NO_2 concentrations are essentially independent of initial hydrocarbon input [3]. However, two other studies imply that hydrocarbon reductions decrease maximal NO_2 concentrations. The UNC outdoor chamber results indicate that 50% hydrocarbon control tends to decrease maximal NO_2 concentrations by about 10% to 20% [1]. The General Motors chamber studies indicate that 50% hydrocarbon control reduces maximal NO_2 by about 25% [4]. These latter two studies also show that maximal NO_2 is relatively more sensitive to hydrocarbon reductions at higher NO_x levels.

7.1.3 Summary of Chamber Results

All of the chamber experiments agree concerning the proportional dependence of NO_2 (average or peak concentrations) on NO_x. These studies also concur that hydrocarbon control will reduce maximal NO_2 concentrations relative to average NO_2 concentrations. The disagreement concerns exactly how this relative change in maximal and mean NO_2 will occur. The Bureau of Mines study (and Stephens' hypothesis) indicate that hydrocarbon control would leave maximal NO_2 unchanged but would increase average NO_2. The UNC and General Motors studies indicate that hydrocarbon control would reduce maximal NO_2 but would yield no change (or a slight benefit) in average NO_2.

Considering the results of all the chamber studies, it is possible to arrive at an overall best estimate of the effect of hydrocarbon control on NO_2 concentrations. The consensus based on existing chamber results would appear to be as follows: Fifty-percent hydrocarbon control would have little effect on average NO_2 concentrations, a change of ± 10%, but would yield moderate benefits in terms of maximal NO_2, a reduction of about 10% to 20%.

7.2 FORMULATION OF EMPIRICAL MODELS

Empirical models, based on statistical analysis of ambient data, should be able to further our present understanding of the NO_2/precursor dependence. Where the various chamber studies appear to reach a consensus, empirical models can verify that the conclusions are representative of the real atmosphere. Where the individual chamber studies disagree, empirical models may help to resolve the discrepancies.

Developing empirical models for annual average NO_2 and yearly one-hour maximum NO_2 is a complex procedure. Some of the complications become apparent if the typical diurnal pattern of nitrogen dioxide, shown in Figure 7.9, is considered. Figure 7.9 demonstrates that ambient NO_2 concentrations tend to peak twice during the day--once in the late morning and once in the evening. The exact times and relative strengths of these peaks vary from day to day and depend on the season and geographic location. The yearly maximum one-hour concentration in the morning is often about the same as the yearly one-hour maximum in the evening. Thus, in general, an empirical model relating precursors to yearly one-hour maximum NO_2 should consider both the morning and evening peaks. Figure 7.9 also demonstrates that the minimal NO_2 concentrations, which occur in the early morning and late afternoon, are not negligible compared with the maximal concentrations. This phenomenon warrants the conclusion that an empirical model for annual average NO_2 must include all hours of the day, not just the times of peak concentrations.

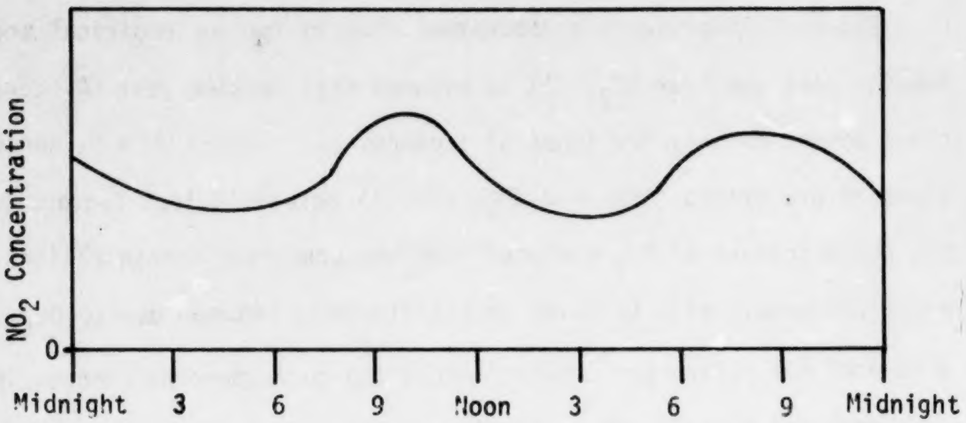

Figure 7.9 Typical **Diurnal** Pattern for Nitrogen Dioxide

In formulating empirical models for the NO_2/precursor dependence, it is convenient to divide each day into two periods: "daytime", from 6:00 A.M. to 4:00 P.M.; and "nighttime", from 4:00 P.M. to 6:00 A.M. Empirical models for each time period would be based on observed relationships between daily NO_2 concentrations and daily precursor concentrations at the beginning of that time period. For instance, the "daytime" peak one-hour NO_2 and "daytime" average NO_2 might be related to 6:00-9:00 A.M. concentrations of hydrocarbons and NO_x. The "nighttime" peak one-hour and average NO_2 concentrations might best be related to 4:00-7:00 P.M. NO_x and, possibly, to late-afternoon oxidant. Interactions between the two time periods should also be investigated. For instance, morning hydrocarbon concentrations might be inversely related to nighttime NO_2, since low HC concentrations would tend to suppress reactions that consume NO_2. Also, leftover NO_2 from the nighttime period may significantly affect the NO_2 levels of the subsequent "daytime" period.

7.2.1 Alternative Model Formulations

Figure 7.10 presents a conceptual diagram for an empirical model of daytime peak one-hour NO_2. It is assumed that daytime peak NO_2 concentrations depend on only two types of factors: (1) 6:00-9:00 A.M. concentrations of precursors (NMHC and NO_x); and (2) meteorological factors that govern the concentration of NO_2 produced from the precursor concentrations. The empirical models will be based on relationships between day-to-day changes in 6:00-9:00 A.M. precursor concentrations and corresponding changes in daytime peak one-hour NO_2 concentrations. Day-to-day changes in precursor concentrations are produced by several processes, including variance in overnight and early-morning dispersive conditions, weekday/weekend emission changes, variance in overnight air mass trajectories (and associated stationary source areas), and changes in vehicular emission factors induced by variance in temperature and humidity. The first process, dispersion, is the dominant factor changing precursor concentrations from day to day. The last two processes are notable because they affect the NMHC/NO_x ratio as well as overall NMHC and NO_x concentrations. The empirical approach followed here implicitly assumes that daily changes in precursor concentrations, produced mostly by overnight and early-morning meteorological variance, can be used to model the effect of changes in precursor concentrations that would result from control strategies.

The most simplistic statistical analysis that could be performed on the system in Figure 7.10 would be to determine the function

$$\text{Daytime Peak One-Hour } NO_2 = F_1(\text{NMHC}, NO_x) , \tag{1}$$

where NMHC = 6:00-9:00 A.M. NMHC concentration,

and NO_x = 6:00-9:00 A.M. NO_x concentration.

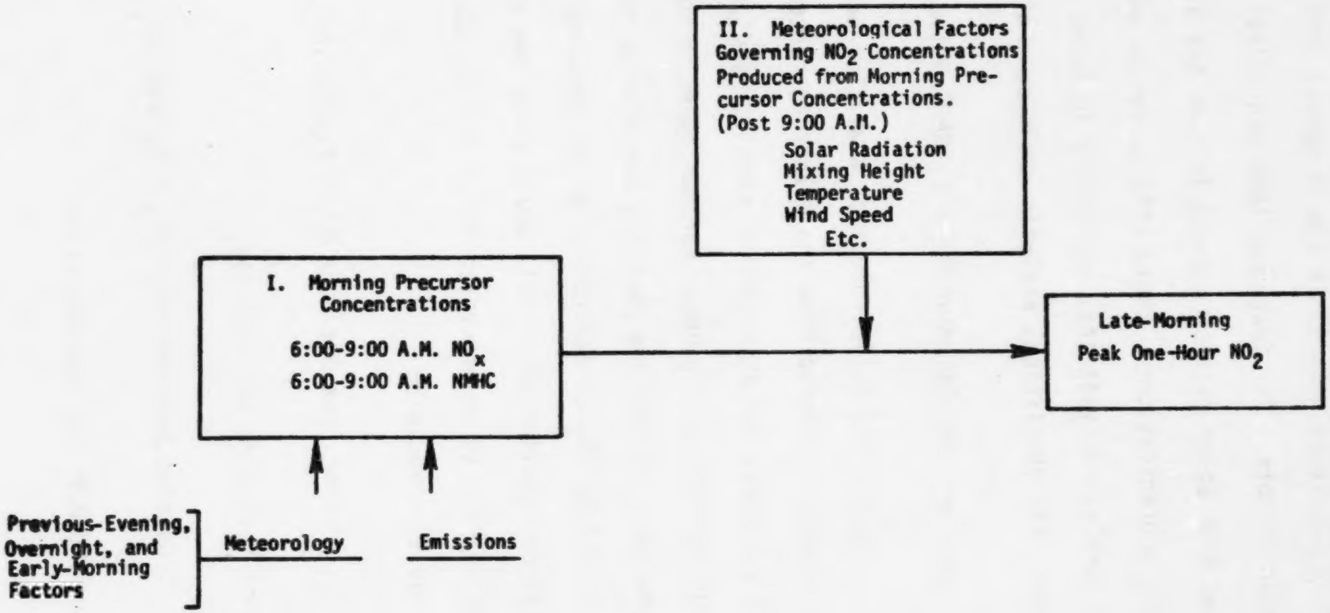
I. Morning Precursor Concentrations
6:00-9:00 A.M. NO_x
6:00-9:00 A.M. NMHC
II. Meteorological Factors Governing NO_2 Concentrations Produced from Morning Precursor Concentrations. (Post 9:00 A.M.)
Solar Radiation
Mixing Height
Temperature
Wind Speed
Etc.
Late-Morning Peak One-Hour NO_2
Previous-Evening, Overnight, and Early-Morning Factors
Meteorology
Emissions

Figure 7.10 Conceptual Diagram of Empirical Model for Daytime Peak One-Hour NO_2

The function, F_1, would form the basis for an empirical model for daytime peak NO_2 by indicating the percentage change in peak one-hour NO_2 that would be attained from various percentage changes in NMHC and NO_x concentrations.

One of the major drawbacks of the simplistic approach is that the relationship between peak one-hour NO_2 and precursors (i.e., Equation (1)) might be spurious in the sense that it is due to mutual correlations with unaccounted for weather factors. For instance, NMHC concentrations might be positively correlated with solar radiation, which in turn has a positive relationship to peak NO_2 concentrations. These effects can be partially discounted for by a more complex analysis that explicitly includes the weather factors. In this case, the statistical analysis would determine the equation

$$\text{Daytime Peak One-Hour } NO_2 = F_2(NMHC, NO_x, W_1, \ldots, W_N) , \qquad (2)$$

where $W_1, \ldots, W_N$ are the daily values of N weather parameters that govern NO_2 concentrations produced from the precursor concentrations. Equation (2) would form the basis for an empirical model by indicating the net effect of precursor changes on NO_2 under various types of meteorological conditions.

The analysis for daytime peak NO_2 can also be made more complex by including 5:00 A.M. NO_2 concentration as an independent variable in Equation (1) or Equation (2). This would allow the carry-over effect of previous-day NO_2 to be accounted for. In this case, the basic empirical equation would be

$$\text{Daytime Peak One-Hour } NO_2 = F_3(NMHC, NO_x, NO_2^*), \qquad (3)$$

or if weather variables are included,

$$\text{Daytime Peak One-Hour } NO_2 = F_4(NMHC, NO_x, W_1, \ldots, W_N, NO_2^*) \qquad (4)$$

where $NO_2^* = 5{:}00$ A.M. NO_2 concentration.

Empirical models based on Equation (3) or (4) would require coupling with a model for overnight NO_2. That is, the dependence of 5:00 A.M. NO_2 on previous-day precursors (NMHC and NO_x) would have to be included before Equation (3) or (4) could be used to represent the full dependence of daytime peak NO_2 on primary pollutants.

Empirical models for daytime average NO_2 are obtained simply by taking average NO_2 rather than one-hour peak NO_2 as the dependent variable in Equations (1) through (4). Similar empirical models can be formulated for nighttime peak one-hour NO_2 and nighttime average NO_2. For the nighttime case, the averaging times for precursor concentrations and weather variables would, of course, be different from the averaging times for the daytime case. Also, late-afternoon oxidant might be included as a "precursor" variable for nighttime NO_2. An assumed relationship of oxidant versus NMHC and NO_x would then be required to translate the dependence of NO_2 on oxidant into a dependence of NO_2 on primary precursors.

7.2.2 Study Areas

The empirical modeling analysis will be conducted for 8 locations. Two of these, Denver and Chicago, are center-city CAMP sites, operated by the United States Environmental Protection Agency. Two other sites are in Houston, Texas: the Mae Drive site (near the main source area of Houston) and the Aldine site (about ten miles downwind of the main source area). The other 4 sites are in Los Angeles County and are operated by the Southern California Air Quality Management District. The Los Angeles County sites were selected so that 1 (Downtown Los Angeles) is in the center of the county, 1 (Lennox) is in the coastal upwind portion of the county, and 2 (Azusa and Pomona) are in the inland downwind portion of the county. These 4 sites and the typical wind patterns in the Los Angeles basin are shown in Figure 7.11

The complexity of the empirical models selected for each location (e.g., whether meteorological parameters are included), will depend on data availability. For the present study, comprehensive data are available for pollutant and weather variables at 1 location (Downtown Los Angeles). Several empirical models with varied degrees of complexity will be applied to that location. The results of the alternative models will be compared, and an assessment will be made of the adequacy of very simple models (e.g., Equation (1)). Applications to locations other than Downtown Los Angeles will be restricted to simple models because meteorological data are not readily available for the other locations.

7.2.3 Combination of Submodels

In this study, the empirical modeling analysis will be disaggregated by season. As discussed in Chapter 9, diurnal patterns for nitrogen dioxide show marked seasonal changes, especially from summer months to winter months. It is interesting to determine if the NO_2/precursor relationship also undergoes substantial seasonal changes. Disaggregating the analysis by seasons also tends to keep weather factors more uniform in each analysis. This disaggregation should reduce the problem of spurious relationships due to hidden correlations between precursor concentrations and weather factors that govern NO_2 production from the precursors.

To construct complete empirical models for annual average NO_2 and yearly peak one-hour NO_2 requires a synthesis of the individual models for

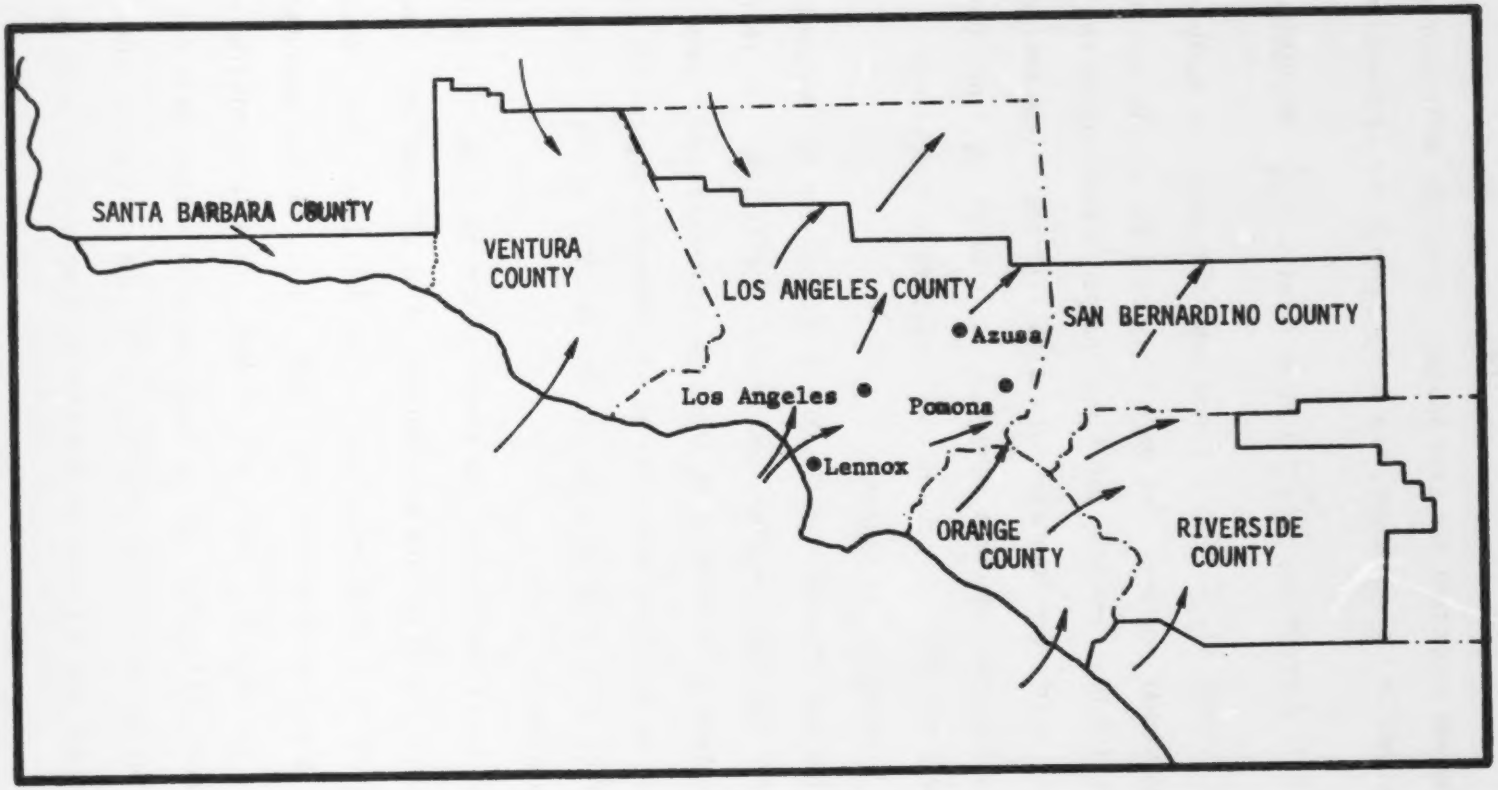
SANTA BARBARA COUNTY
VENTURA COUNTY
LOS ANGELES COUNTY
SAN BERNARDINO COUNTY
Azusa
Los Angeles
Pomona
Lennox
ORANGE COUNTY
RIVERSIDE COUNTY

Figure 7.11 Map of the Metropolitan Los Angeles AQCR

daytime and nighttime for each season. Using the definition of "daytime" and "nighttime" given above, the daily average for each season is given by

$$\text{Daily Average NO}_2 = \frac{10}{24} \cdot \text{Daytime Average} + \frac{14}{24} \cdot \text{Nighttime Average}. \quad (5)$$

Yearly average NO_2 is just a linear combination of the daily averages for the individual seasons. The empirical model for yearly one-hour maximum NO_2 will be the peak one-hour model for the particular season and time of day when the yearly one-hour maximum occurs. If the yearly maximum can occur in more than one season or more than one time of day, then two or more submodels for peak one-hour NO_2 will have to be considered.

7.2.4 Limitations of Approach

The specific empirical models proposed here for determining the NO_2/precursor dependence suffer from several limitations. It is implicitly assumed that daily changes in precursor concentrations, produced mostly by variance in overnight and early-morning meteorology, can be used to model the effect of control strategies. The validity of this assumption has not been resolved.

As noted previously, the simple models that omit meteorology may result in correlations which are not representative of causality. The more complex models require a detailed meteorological data base. Data requirements may present a problem even with the simple models, because measurements are needed each day for NO_2, NO_x, NMHC, and oxidant. Because of missing values for one or more pollutants, two to three years of ambient data are often necessary to provide an appropriate sample size for the statistical analyses. The data requirements are worsened by the need to sample over a wide range of $NMHC/NO_x$ ratios.

Another limitation of the empirical models used here is the neglect of precursor emissions that occur after the time when ambient precursors are measured. For example, in the daytime NO_2 model, the 6:00-9:00 A.M. precursor concentrations represent emissions only up to 9:00 A.M. This limitation may not be extremely serious because accumulated overnight and early-morning emissions (up to 9:00 A.M.) are substantially larger than the total amount of late-morning emissions. Also, the day-to-day variations in 6:00-9:00 A.M. concentrations may be somewhat representative of day-to-day variations in precursor concentrations resulting from late-morning emissions.

Perhaps the most serious drawback of our approach is the neglect of transport. Nitrogen dioxide concentrations will be related to precursor concentrations measured at the same location but at an earlier time. If significant transport occurs, the nitrogen dioxide measurements and precursor measurements will be associated with totally different air masses. This could destroy the possibility of obtaining the desired relationships. For the case of peak NO_2 concentrations in the Los Angeles basin, there is reason for encouragement because the times between the precursor measurements and NO_2 peaks (approximately 9:00 A.M. to 10:00 A.M. and 7:00 P.M. to 10:00 P.M.) tend to be periods of stagnation[8,9]. For other cities and for average NO_2 concentrations, transport may be a very important problem. This problem should be kept in mind when reviewing the results of the models applied in this study.

It is possible to formulate more complex empirical models that can take into account emissions from all hours[10,11] and that do include pollution transport[11,12]. However, formulating and applying these complex models requires much greater effort and is beyond the resources of the present investigation.

The limitations of the empirical approach taken here can have considerable impact on the relationships observed between ambient NO_2 and ambient precursor concentrations. For example, assume that NO_2 concentrations are, in actuality, directly proportional to NO_x input. If transport were a very significant factor, regressions of daytime NO_2 concentrations versus early-morning NO_x concentrations may show little or no dependence because the two measurements are associated with different air masses. In this case, the statistical relationship between NO_2 and NO_x would entirely misrepresent the causal dependence.

Because of the limitations in our approach, it may not be possible to arrive at purely statistical formulas that precisely represent the dependence of NO_2 on its precursors. At the minimum, however, the empirical models should indicate the important qualitative aspects of the NO_2/precursor relationship (such as whether a hydrocarbon dependency exists). These conclusions can be checked against historical trends in precursors and NO_2. In the end, control strategy analysis might best be performed by combining the results of the empirical models with the findings of smog-chamber tests.

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8.0 PREPARATION OF DATA BASE FOR EMPIRICAL MODELING

The objective of Part II of this project is to determine how peak and average NO_2 concentrations depend on precursor concentrations. The data base consists of hourly readings of NO, NO_2, NO_x, HC, CH_4, NMHC, and oxidant at 2 CAMP monitoring sites (Chicago and Denver), 2 Houston sites (Mae and Aldine), and 4 Los Angeles basin sites (Downtown Los Angeles, Lennox, Azusa, and Pomona). At 1 of the Los Angeles sites, Downtown Los Angeles, detailed meteorological data are also included. The Chicago and Denver data were obtained from EPA's SAROAD system; the Houston data, from the Texas Air Control Board (TACB); and the Los Angeles data, from the Southern California Air Quality Management District (SCAQMD).

Chicago, Denver, and Los Angeles were selected as three cities providing long-term air quality data and representing a range of climatic conditions. Although Houston has only a short history of air quality data, it was included because of the possibility of special conditions in Texas[1,2]. Because of its numerous air monitoring stations, the Los Angeles area is very suitable for study of intraregional patterns in the NO_2/precursor dependence; therefore, we have included 4 SCAQMD sites in the analysis.

This chapter documents the procedures used to process and check the raw data. Section 8.1 describes the original data base; Section 8.2 indicates how the raw data were organized into a processed data base; and Section 8.3 discusses the data quality check. These efforts culminated in the creation of an edited data base with a convenient format for statistical studies.

8.1 COMPUTER TAPES OF AEROMETRIC DATA

Magnetic tapes of hourly air quality data from the Denver and Chicago CAMP sites were obtained from the SAROAD system. Although these tapes covered the period 1963 to 1973, only five years of data (1969 to 1973) were employed in the statistical study. Restricting the analysis to five years provided sufficient data for the empirical models and limited the cost of data processing. Table 8.1 lists the pollutants and monitoring methods for Denver and Chicago.

Table 8.1 Pollutant Data Used for Denver and Chicago

Pollutant	Method	SAROAD Code (Pollutant-Method)
NO	Colorimetric	42601-11
NO_2	Colorimetric-Griess-Saltzman	42602-12
NO_x	($NO + NO_2$)	--
OX	Colorimetric Neutral KI	44101-14
HC	Flame Ionization	43101-11
CH_4	Flame Ionization	43201-11
NMHC	($HC - CH_4$)	--

The hourly data on the SAROAD tapes was listed in an 80-column (card-image) format as described in Table 8.2. Missing values were represented by blanks. The original SAROAD tapes were organized according to the following order: station, pollutant, year, and day. The units of all the pollutants were ppm.

Table 8.2 Format of Hourly SAROAD Data for CAMP Sites

Column	Entry	Column	Entry
1	1	21,22	Sampling start hour (standard time), either 0:00 or 12:00
2,3	State	23-27	Parameter identification
4-7	Area	28,29	Method identification
8-10	Site	30,31	Unit code
11	Agency type	32	Decimal locator
12,13	Project classification	33-36	Observed values, in chronological sequence. Position of entry indicates time of observation (0:00-1:00, 1:00-2:00, etc.) in standard time
14	Sampling time interval	37-40	
15,16	Year	Etc.	
17,18	Month	77-80	

The data for the Houston/Mae and Houston/Aldine sites were provided through the courtesy of the Texas Air Control Board. These data covered the years 1974 through 1976. However, monitoring for NO (and total NO_x) began in March 1975 at the Houston sites. Thus, data from only March 1975 to December 1976 were useful for the present study. Table 8.3 lists the pollutants and monitoring methods for the Mae and Aldine locations.

Table 8.3 Pollutant Data Used for Houston/Mae and Houston/Aldine

Pollutant	Method	SAROAD Code (Pollutant-Method)
NO	Chemiluminescence	42601 - 14
NO_2	Chemiluminescence	42602 - 14
NO_x	$(NO + NO_2)$	42603 - 14
O_3	Chemiluminescence	44201 - 11
HC	Flame Ionization	43101 - 11
CH_4	Flame Ionization	43201 - 11
NMHC	$(HC - CH_4)$	43102 - 11

The hourly data for Houston were organized in the SAROAD format illustrated in Table 8.2. The units of all pollutants were ppm. The Houston data were organized according to the following order: year, station, pollutant, day.

Data tapes for Los Angeles sites had been obtained earlier by Technology Service Corporation from the Los Angeles section of the Southern California AQMD.* Although these tapes covered the period 1955 through August 1974, only data taken after 1969 were used in the statistical study. Table 8.4 lists the pollutants used in the statistical analysis.

Table 8.5 presents the format for the hourly APCD data. As with the SAROAD tapes, missing data were represented by blanks for the Los Angeles sites. The original APCD data were organized according to pollutant, station, year, and day.

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*Most of these data, except for methane, are also available from SAROAD or from the California Air Resources Board.

Table 8.4 Pollutant Data Used for the 4 Los Angeles Sites

Pollutant	Method	APCD Code
NO	Colorimetric	25
NO_2	Colorimetric	21
NO_x	$(NO + NO_2)$	--
OX	Colorimetric KI	39
HC	Flame Ionization	31
CH_4	Flame Ionization	32
NMHC	$(HC - CH_4)$	--
CO	Nondispersive Infrared	15
SO_2	Coulometric	18

Table 8.5 Format of Hourly APCD Data

Column	Entry	Column	Entry
1	Dele. Code	22-24	Hourly readings, 3 spaces each
2-4	Variable	25-27	The position of an entry defines the time of the reading, 0:00-1:00, 1:00-2:00,..., 23:00-24:00, standard time.
5-8	Station	28-30	
9-12	Year	⋮	
13-14	Month	91-93	
15,16	Days in month	94-97	Daily average
17,18	Day	98-100	Number of hourly readings
19	Day of week	101-103	Maximum hourly reading
20	Holiday	104-106	Instantaneous maximum
21	No-data day	107,108	Hour of occurrence of inst. maximum
		. . . .	Each day continues as above until the end of the month. Then there is a list of various averages and other statistics pertaining to that month.

Meteorological data tapes, in the form of the APCD "99 Cards," were also available for Downtown Los Angeles. Table 8.6 lists the parameters included on the meteorological data tapes.

Table 8.6 Parameters Included in the APCD Meteorological "99 Cards" for Downtown Los Angeles

Parameter

1. Maximum oxidant value in Los Angeles County and station where maximum oxidant occurred
2. Maximum degree of eye irritation and time of occurrence
3. Minimum recorded visibility and related data
4. Minimum relative humidity from 6:00 to 19:00
5. Maximum temperature
6. Average wind speed, 6:00-12:00
7. Hourly wind directions
8. Average wind speed, 6:00-9:00

Parameter

9. Inversion base height at 4:00 or 7:00
10. Various parameters describing the 4:00 or 7:00 inversion
11. Calculated maximum mixing height for the day
12. Parameters describing 850 pressure level
13. Pressure gradient (LAX to Palmdale) at 7:00
14. Temperature gradient (LAX to Palmdale) at 7:00
15. Accumulated solar radiation, 7:00-12:00

8.2 CREATION OF THE PROCESSED DATA BASE

The first part of the data-processing task was to reorganize the original data into a more practicable format for the statistical studies. Since the original tapes were organized first by pollutant and then by day, the air pollution readings for any given day were scattered over the tapes. The data were reorganized so that all pollution data for each day are grouped together. In this new format, each day on the tape is followed by the subsequent day. The new, reorganized data tapes were then used with a simple data retrieval program to generate printouts in the format illustrated in Table 8.7. With the new format, one could quickly visually examine all pollutant data for a given day. Also, the new tape format greatly simplifies data retrieval for the statistical analysis.

Table 8.7 New Format for Pollutant Variables

STATION

DATE Year | Month | Day

READING NUMBER ...	1	2	3	....	24
(STANDARD TIME)...	(0:00-1:00)	(1:00-2:00)	(2:00-3:00)	....	(23:00-24:00)
NO	X	X	X	....	X
NO_2	X	X	X	....	X
HC	X	X	X	....	X
CH_4	X	X	X	....	X
OX	X	X	X	....	X
NO_x	X	X	X	....	X
NMHC	X	X	X	....	X
SO_2[*]	X	X	X	....	X
CO[**]	X	X	X	....	X
APCD 99 CARD VARIABLES[**]	X	X	X	....	

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[*] Los Angeles stations only

[**] Downtown Los Angeles only

The "first generation" processed data base included many days with incomplete data. The next task was to develop a "second generation" processed data base which excluded days with grossly incomplete data. For this task, we composed six completeness criteria and determined, for each site, the number of summer and winter days meeting each criterion.* We hoped to choose a criterion that would strike a balance between quantity and quality; i.e., we wished to retain as many days as possible while restricting ourselves to days with rather complete data.

The selection criteria were based on our interest in certain times of the day for which we needed precursor or NO_2 data for the empirical models. the periods (in civil time) were

- hydrocarbons (preferably nonmethane): 6-9 A.M. (readings 7,8, & 9 in standard time readings 6,7 & 8 daylight time)
- oxides of nitrogen: 6-9 A.M. plus 3-7 P.M.
- oxidant or ozone: 2-5 P.M.
- nitrogen dioxide: 6 A.M. of the first day to 6 A.M. of the next day with emphasis on readings at 4-6 A.M., 9-12 A.M., and 4-7 P.M.

These times can be called the "fields of interest."

The first selection criterion (1A) required essentially complete data within the fields of interest and allowed only one-hour gaps in the NO_2 record for the day. This strict criterion involved the following specific restrictions:

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*"Summer" was taken as April-September, "winter" as October-March.

1A. NMHC: all 3 readings from 6-9 A.M.

OX: at least 2 readings from 2-5 P.M.

NO_2: all 3 readings from 9-12 A.M.

all 3 readings from 4-7 P.M.

at least 1 reading among 4-6 A.M.

Not more than 1 consecutive missing value from 6 A.M. of the first day to 6 A.M. of the next day

NO_x: all 3 readings from 6-9 A.M.

all 4 readings from 3-7 P.M.

All times were in civil time (daylight time from May through October and standard time from November through April).

Criterion 1B was the same as 1A except the NMHC restriction was changed to a THC restriction. A separate criterion was formulated for THC because preliminary investigations indicated that some CAMP sites might have considerably more THC data than NMHC data.

Criteria 2A and 2B require that most (but not all) of the data in the fields of interest be present. The specific criteria were:

2A. NMHC: at least 2 readings from 6-9 A.M.

OX: at least 2 readings from 2-5 P.M.

NO_2: at least 2 readings from 9-12 A.M.

at least 2 readings from 4-7 P.M.

No more than 3 consecutive missing values from 6 A.M. to 6 A.M. the next day

NO_x: at least 2 readings from 6-9 A.M.

at least 3 readings from 3-7 P.M.

2B. Same as 2A, except THC is required instead of NMHC.

The weakest pair of criteria, 3A and 3B, allow substantial data gaps in the field of interest, as long as the data are complete enough to permit reasonable "interpolation." Thus, each completeness requirement within the field of interest is replaced by a weaker one, and specifications are added for data which will allow interpolation. Criteria 3A is as follows:

3A. NMHC: at least 1 reading from 6-9 A.M.
at least 2 readings from 5-10 A.M.
OX: at least 1 reading from 2-5 P.M.
NO_2: at least 1 reading from 9-12 A.M.
at least 2 readings from 8 A.M.-1 P.M.
at least 1 reading from 4-7 P.M.
at least 2 readings from 3-8 P.M.
No more than 4 consecutive readings missing from 6 A.M. to 6 A.M. the next day.
NO_x: at least 1 reading from 6-9 A.M.
at least 2 readings from 5-10 A.M.
at least 2 readings from 3-7 P.M.
at least 3 readings from 2-8 P.M.

Criterion 3B is the same as 3A, except THC (not NMHC) readings are required.

The next task was to run a computer program to count, for each site, the number of summer and winter days meeting each criterion. The results are presented in Table 8.8. Predictably, each site showed an increase in sample size as the criteria became less strict (i.e., from criterion 1 to

Table 8.8 Number of Days Meeting Each Criterion

	Criterion Number					
	1A	**1B**	**2A**	**2B**	**3A**	**3B**
Chicago						
summer	68	271	138	398	162	455
winter	79	288	124	386	140	415
Denver						
summer	133	143	221	242	277	305
winter	193	222	330	345	427	436
Houston/Mae						
summer	74	74	94	94	105	105
winter	41	41	58	58	62	62
Houston/Aldine						
summer	47	47	63	63	67	67
winter	60	60	77	77	83	83
Los Angeles						
summer	471	474	713	716	839	842
winter	400	403	636	639	783	785
Lennox						
summer	419	424	624	632	746	757
winter	181	184	520	523	652	655
Azusa						
summer	522	523	683	684	742	742
winter	429	429	591	592	637	637
Pomona						
summer	529	532	752	752	801	801
winter	464	472	662	663	677	677

Note: "Summer" is defined as April through September.
"Winter" of a given year is January through March, plus October to December.

2 to 3). With the exception of Chicago, each site provided nearly as many days meeting the NMHC criteria as the HC criteria. However, because of spotty methane data, Chicago had many more days meeting the "B" criteria than the "A" criteria. The low number of days in Houston for all criteria results from the limited duration of sampling (March 1975-December 1976).

To create the processed data base, we decided to choose criterion 2A for all sites except Chicago, where we selected criterion 2B. Choosing criterion 2 allowed us to maintain a sufficiently large data base for the empirical models. Although criterion 3 would have yielded an even larger data base, it was rejected as permitting too much interpolation and lowering the quality of the data. Criterion 1 was rejected as leaving too little data for certain cities.

One subtlety in the compilation of the data base was the distinction between ozone (O_3) and oxidant (OX). The 2 Houston sites measure ozone according to the chemiluminescence method. Although the 6 CAMP and Los Angeles sites measure total oxidant by the potassium iodide (KI) method, the 2 CAMP sites actually report O_3 by correcting for NO and NO interference according to the equation

$$[O_3] = [OX] - 0.2[NO_2] - 0.2[NO]. \qquad (6)$$

During the years of interest, the oxidant monitors at the CAMP sites were fit with SO_2 scrubbers, and the above interference correction is appropriate for such monitors[3,4,5].*

The Los Angeles oxidant monitors are not equipped with SO_2 scrubbers. A different interference correction is appropriate for these sites[4,6]:

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*Note that the SO_2 scrubbers convert NO to NO_2.

$$[O_3] = [OX] - 0.2[NO_2] + [SO_2] \qquad (7)$$

This correction has not been applied by the Los Angeles AQMD because NO_2 and SO_2 are generally negligible when ozone is high[7]. However, at night and at other low-ozone periods, the negative contributions of SO_2 and the positive contribution of NO_2 can be quite significant. For consistency with Chicago and Denver, we decided to correct all Los Angeles area oxidant readings for NO_2 and SO_2 interference, using Equation (7). During the afternoon oxidant peak, this correction appears reasonable; however, one must use caution in correcting the low oxidant readings of 1 pphm (the minimum reported) encountered at other times. In these cases, the number generated by adding SO_2 to oxidant may exceed the actual ozone level. For example, an ozone value of 2 pphm and a SO_2 reading of 4 pphm would cause a minimum oxidant reading of 1 pphm to be corrected to 5 pphm, more than twice the actual ozone level. Thus, in cases where oxidant is reported as 1 pphm, there is uncertainty as to the real ozone level.

8.3 DATA QUALITY CHECK

The Los Angeles and Houston air quality data are subject to extensive quality control procedures and are thoroughly screened before publication[8,9].* In contrast, the post-1969 CAMP data for Denver and Chicago have been subject to little quality control beyond a cursory inspection[5]. Therefore, our quality control and editing efforts focused on the Denver and Chicago data bases.

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*We screened all of the Houston data and some of the Los Angeles data ourselves and found no severe anomalies. We also found that the daily pollutant patterns made good sense from a physico-chemical viewpoint.

The first step in the data quality check for Denver and Chicago was to list, for each pollutant, the diurnal patterns for the five days per year with the highest pollution levels. We scanned these visually to determine: (1) whether the maximum concentrations reported for each pollutant were reasonable and were consistent with other pollutants; and (2) whether there were any unusually abrupt concentration changes between consecutive readings.

Next, the entire processed data base (grossly incomplete days excluded by the criteria chosen in Section 8.2) was reviewed for reasonableness and consistency among pollutant readings. The following checks were then applied:

- The hourly pollution values were scanned, and any sharp rises or drops between consecutive readings were scrutinized. Deletions or changes were made when appropriate.
- Oxidant values were compared against the normal pattern of low nighttime levels and higher afternoon concentrations. Days with inexplicably high (>10 pphm) nighttime OX values were deleted.
- The relationships between NO and OX levels were noted. Since these pollutants should not coexist at high concentrations, we calculated the product [OX] x [NO]. Where [OX] x [NO] exceeded 100 pphm^2, the OX and NO values were regarded as suspect [10].
- Days with high NO_2 levels were examined to verify that these were preceded by moderate or high NO levels.
- We deleted a few days in which the intermittency of readings caused us to suspect the validity of the data.

- A check was made for negative NMHC values, which represent the physically impossible situation of the CH_4 concentration exceeding that of total hydrocarbons. Any day with several NMHC readings of less than -2 pphm was deleted as having suspicious HC data. All negative NMHC readings in the "field of interest" were deleted.

- Days with a substantial majority of zero entries for one or more pollutants were deleted on the grounds that the zeroes might actually be missing data.

Table 8.9 lists the days eliminated from the processed data base along with the justification for their deletion. In addition to these deletions, we altered one reading, the 9:00-10:00 A.M. NO_2 reading at Denver on 24 February 1971. Most of the NO_2 readings that day were less than 7 pphm, except for a single value of 37 pphm. We changed that value to 4 pphm, the mean of the preceding and following levels.

It should be noted that Table 8.9 applies only to the processed data base and cannot be considered as a complete list of corrections to the Chicago and Denver CAMP data. There were also obvious problems on many of the days that were eliminated from the processed data base according to the selection criteria. Since these days were already excluded from our study, we did not subject them to the data quality check.

Table 8.9. Deletions Made in Processed Data Bases for Chicago and Denver

City	Date	Reason
Chicago	70-4-22	NMHC << 0
	70-6-22	All entries = 0
	70-12-16	HC = 0
	71-2-18	High O_3 x NO
	71-4-27	Low NO_2, simultaneously high and rising NO + O_3
	72-4-10	OX peaks at 11 P.M.
	72-5-18	NO erratic; NO · OX > 100; OX peak 10 P.M.
	73-2-4	High NO; NO · OX > 100
Denver	72-9-25	NO falls while HC is high, level, and largely missing; no photochemical activity to account for NO falling.
	72-9-4	High NO_2 without prior NO precursor.
	72-10-31	CH_4 and OX - many 0's - could be blanks
	73-7-29	" " " " " " " "
	73-8-22	" " " " " " " "
	73-8-28	" " " " " " " "
	73-8-29	" " " " " " " "
	73-8-30	" " " " " " " "
	73-8-31	" " " " " " " "

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9.0 SEASONAL AND DIURNAL PATTERNS FOR NO_2 AND ITS PRECURSORS

Before the empirical modeling analysis is performed, the seasonal breakdown for the analysis and the averaging times for the pollutant variables must be specified. This chapter arrives at those specifications through an examination of seasonal and diurnal patterns of ambient NO_2, NMHC, NO_x, and oxidant concentrations. Section 9.1 describes seasonal patterns and provides a preliminary recommendation as to the seasonal breakdown. Section 9.2 discusses diurnal patterns during each quarter of the year; this discussion leads to final selections concerning seasons and averaging times. Section 9.3 explains how these selections are used as the basis for a computer file of dependent and independent variables.

9.1 SEASONAL PATTERNS

Figures 9.1 through 9.8 present seasonal pollutant patterns for Denver, Chicago, Houston/Mae, Houston/Aldine, Los Angeles, Lennox, Azusa, and Pomona, respectively. For each location, the monthly averages of daily maximum one-hour concentrations are plotted for NO_2, oxidant,* NO_x, and NMHC (divided by ten). The Denver and Chicago plots represent averages over the period 1969 to 1973; the Houston plots, averages over 1975 to 1976; and the Los Angeles plots, averages over 1969 to 1974.

For each location except Chicago, the primary photochemical precursors (NO_x and NMHC) show pronounced peaks during the winter (1st and 4th quarters), typically reaching a maximum during November or December. These high

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*In the seasonal and diurnal patterns, oxidant measurements (not corrected for interference) are used for the 4 Los Angeles sites. In the empirical models, corrected values representing O_3 will be used.

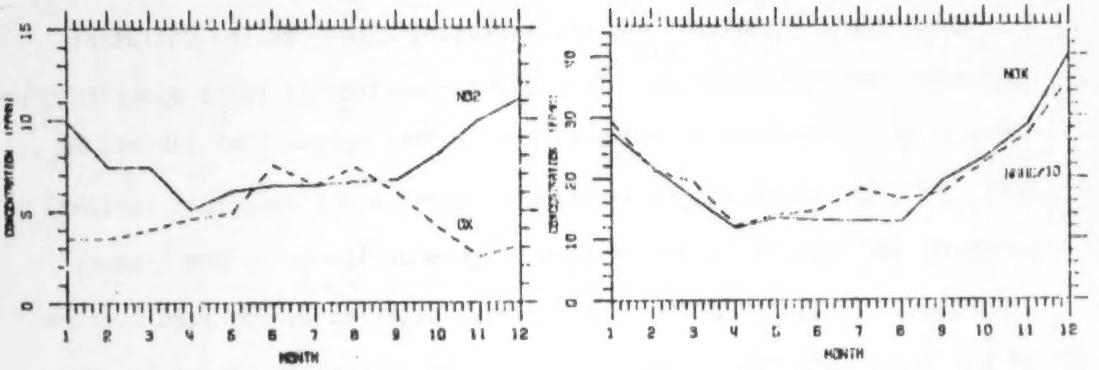

Figure 9.1 Seasonal Pollutant Patterns for Denver
(Monthly Averages of Daily Max One-Hour Concentrations, 1969-1973)

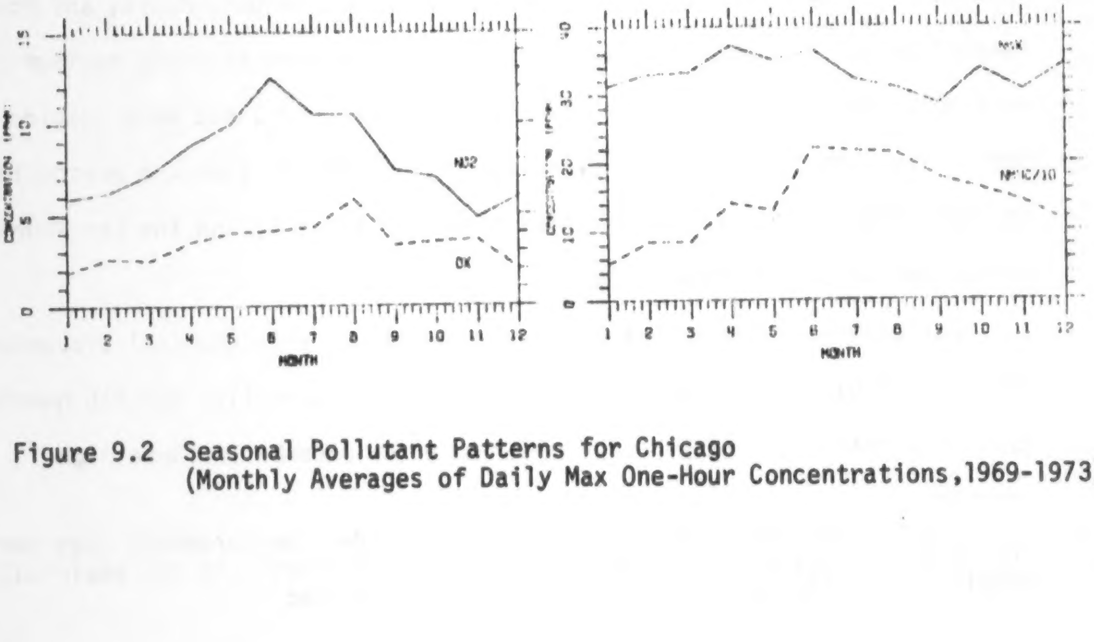

Figure 9.2 Seasonal Pollutant Patterns for Chicago
(Monthly Averages of Daily Max One-Hour Concentrations,1969-1973)

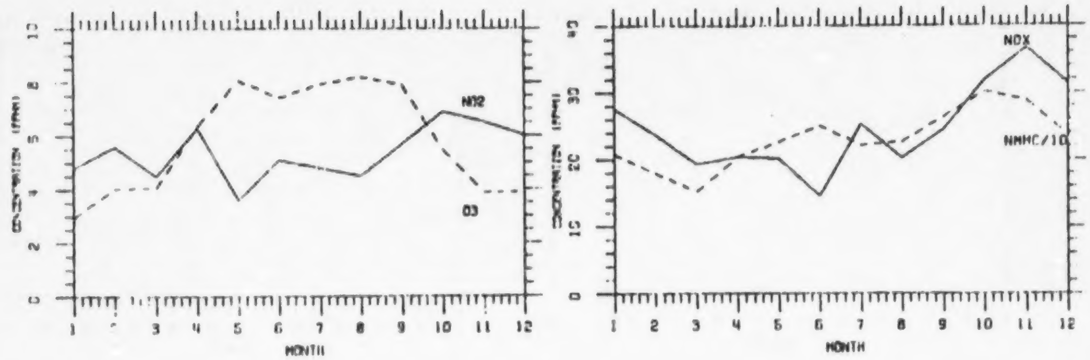

Figure 9.3 Seasonal Pollutant Patterns for Houston/Mae
(Monthly Averages of Daily Max One-Hour Concentrations, 1975-1976)

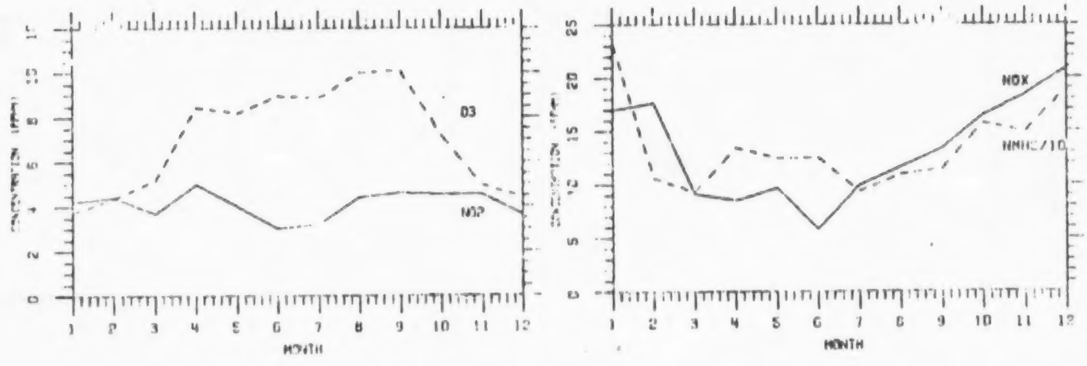

Figure 9.4 Seasonal Pollutant Patterns for Houston/Aldine
(Monthly Averages of Daily Max One-Hour Concentrations, 1975-1976)

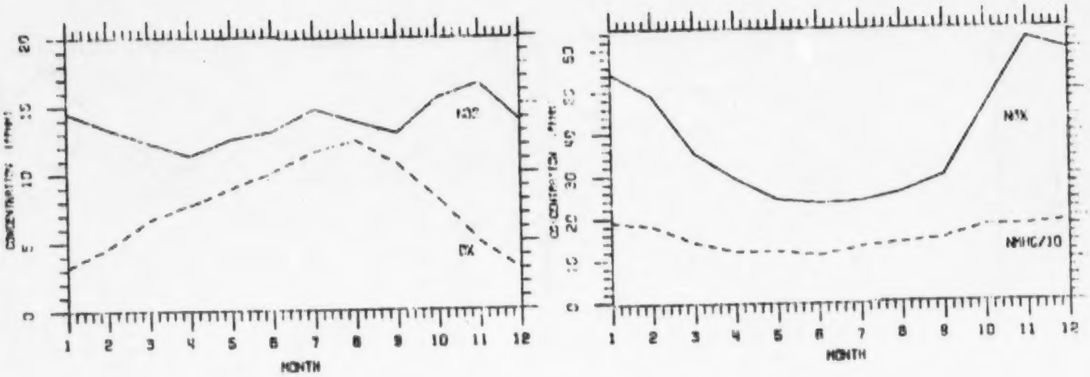

Figure 9.5 Seasonal Pollutant Patterns for Los Angeles
(Monthly Averages of Daily Max One-Hour Concentrations, 1969-1974)

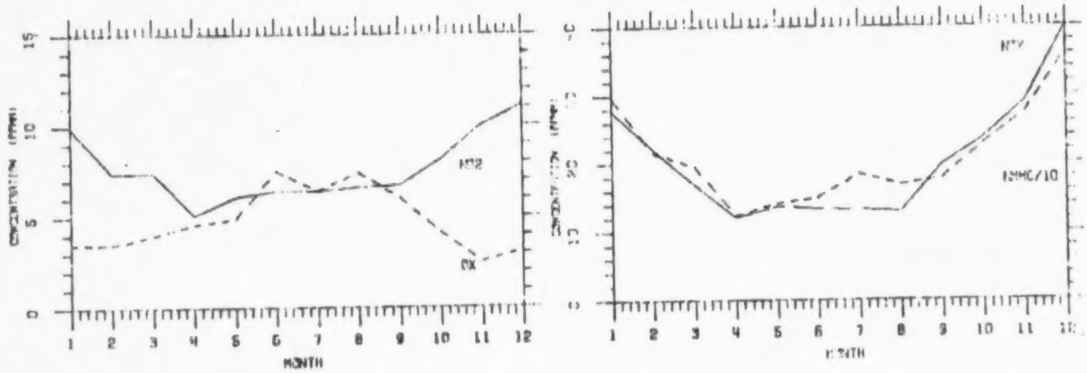

Figure 9.6 Seasonal Pollutant Patterns for Lennox
(Monthly Averages of Daily Max One-Hour Concentrations, 1969-1974)

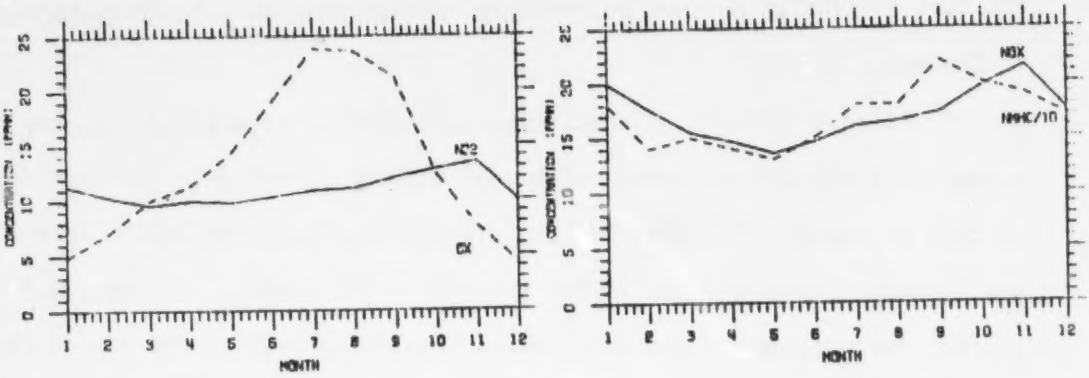

Figure 9.7 Seasonal Pollutant Patterns for Azusa
(Monthly Averages of Daily Max One-Hour Concentrations, 1969-1974)

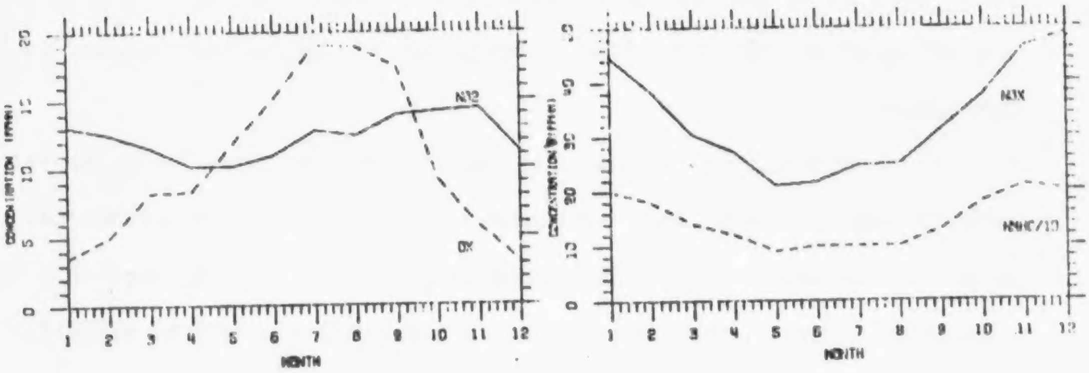

Figure 9.8 Seasonal Pollutant Patterns for Pomona
(Monthly Averages of Daily Max One-Hour Concentrations, 1969-1974)

winter values for the primary contaminants are most likely due to intense nocturnal inversions that tend to occur in the winter. In Chicago, there is no seasonal pattern for NO_x, and NMHC appears to peak in the summer. The last conclusion may not be reliable because NMHC data are very sparse in Chicago.

At all 8 locations, oxidant concentrations are greatest during the summer (2nd and 3rd quarters), with peak oxidant values usually occurring in July or August. Elevated temperature and high solar-radiation intensity are largely responsible for higher oxidant in the summer. In the Los Angeles region, the subsidence inversion which persists throughout the day in the summer also contributes to high oxidant in that season.

Seasonal patterns of nitrogen dioxide concentrations are not consistent among the various locations. Denver and the coastal Los Angeles station (Lennox) experience distinctly higher NO_2 concentrations during the winter. Los Angeles, Azusa, Pomona, and the Houston sites show practically no seasonal pattern in NO_2 levels, although a very minor peak seems apparent in the 4th quarter. Chicago shows a marked peak in NO_2 concentrations during the summer.

It is interesting to note that the seasonal patterns in NO_2 appear to reflect competition between two factors: dispersion and photochemical activity. In the winter there are higher concentrations of NO_x available to produce NO_2, but in the summer there is greater photochemical activity. At Denver and Lennox, primary contaminants show a strong peak in the winter, while oxidant shows a relatively weak summer peak. This may account for NO_2 reaching a peak during the winter at those two stations. At Los Angeles, Azusa, Pomona, and the Houston sites, both the winter primary contaminant peak and the summer oxidant peak are pronounced. This balance may account for the lack of a seasonal NO_2 pattern for those 5 locations. At Chicago, there is no seasonal pattern for NO_x, but the summer oxidant peak still exists. This seems consistent with NO_2 reaching a summer peak in Chicago.

The month-to-month patterns in NO_2, oxidant, NO_x, and NMHC concentrations suggest that at least two seasons can be distinguished. The winter (1st and 4th quarters) is marked by high levels of primary contaminants, while the summer (2nd and 3rd quarters) is marked by high oxidant levels. The empirical modeling analysis should be divided at least once, according to these two seasons. The seasonal division will help to keep weather factors more uniform in the analysis and will also permit an investigation of seasonal changes in the NO_2/precursor dependence.

9.2 DIURNAL PATTERNS

This section analyzes diurnal pollutant patterns for each of the 6 study areas. The diurnal patterns are examined individually for each quarter of the year.* The purpose of the analysis is twofold: (1) to determine if further seasonal breakdowns (beyond the summer/winter division) are called for, and (2) to select appropriate averaging times for the pollutant variables to be included in the empirical models.

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*The quarters are defined as (1) Jan.-Feb.-Mar., (2) Apr.-May-June, (3) July-Aug.-Sept., and (4) Oct.-Nov.-Dec.

Figures 9.9 through 9.16 present diurnal patterns for each quarter of the year at Denver, Chicago, Houston/Mae, Houston/Aldine, Los Angeles, Lennox, Azusa, and Pomona, respectively. Averages for each hour of the day, reported in pphm, are given for NO_2, oxidant, NO_x and NMHC (divided by ten). The 1st and 4th quarters are reported according to standard time, while the 2nd and 3rd quarters are reported in daylight time. Since the hourly data from all 8 cities represent averages from midnight-1:00 A.M., 1:00 A.M.-2:00 A.M., 2:00 A.M.-3:00 A.M., etc., the hourly values are plotted on the half hour, starting at 0:30 A.M.

As evidenced by Figures 9.9 to 9.16, the primary contaminants (NO_x and NMHC) exhibit two peaks during the day. At all the stations and during all seasons, the morning peak tends to occur around 7:30 A.M. or 8:30 A.M. (the 7:00-8:00 A.M. or 8:00-9:00 A.M. hourly average). The morning peak is due to rush-hour traffic and to the low level of atmospheric dispersion that often exists in the early morning. In Denver and Chicago, the evening peak in NO_x and NMHC tends to occur around 5:00-6:00 P.M., reflecting the evening rush hour. The Houston and Los Angeles sites exhibit much later evening peaks, often as late as midnight. The precursor peak occurs this late at Los Angeles sites because atmospheric mixing is quite good in Los Angeles during the afternoon rush hour. The sea breeze is at full strength in the late afternoon, and the inversion is elevated by ground heating. It is not until later in the night, when the sea breeze terminates and a nocturnal inversion begins to take hold, that primary contaminants reach their evening peak in Los Angeles. The late-evening peak at Houston might be explained by similar conditions at that coastal city.

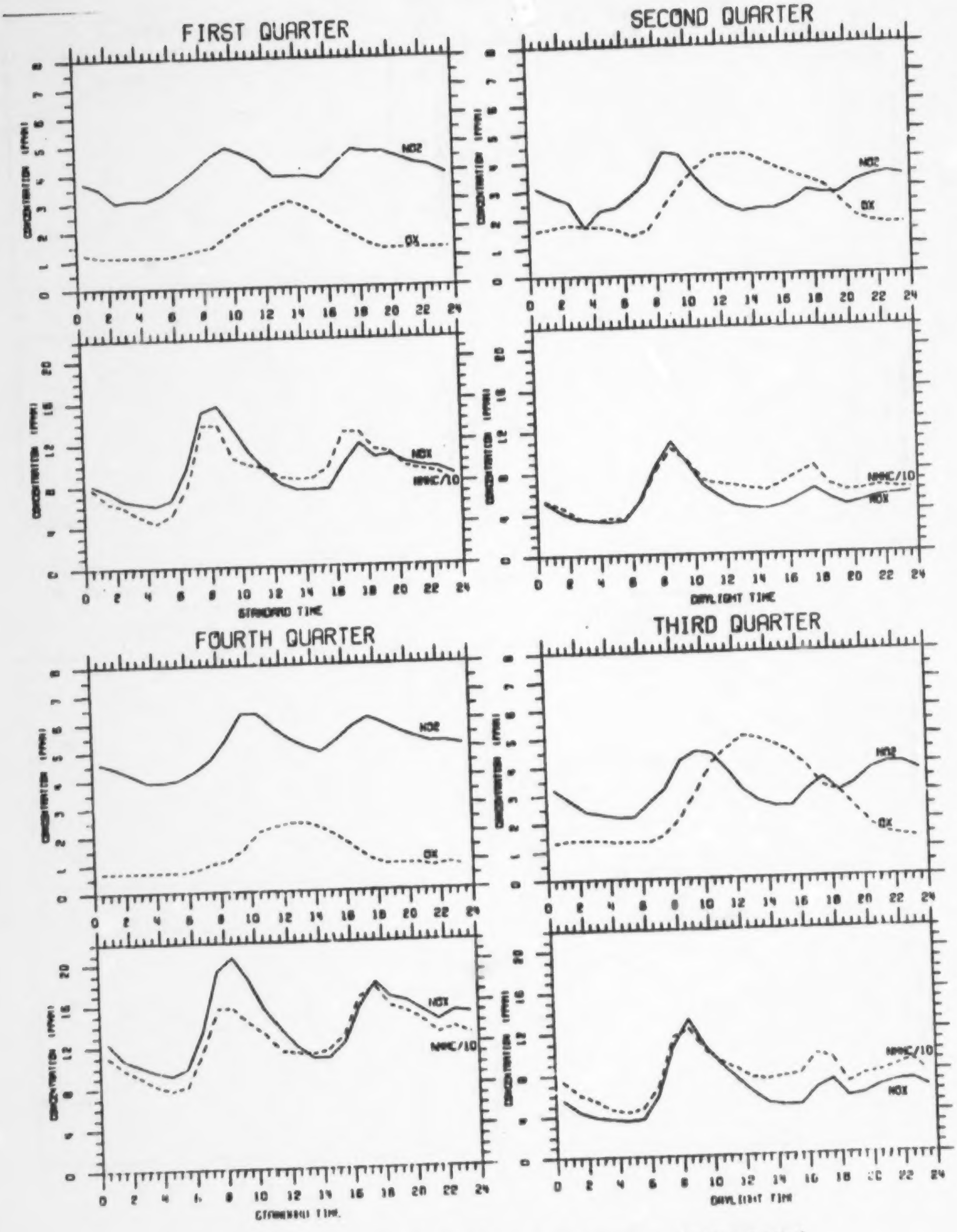


Figure 9.9 Diurnal Patterns at Denver (1969-1973)

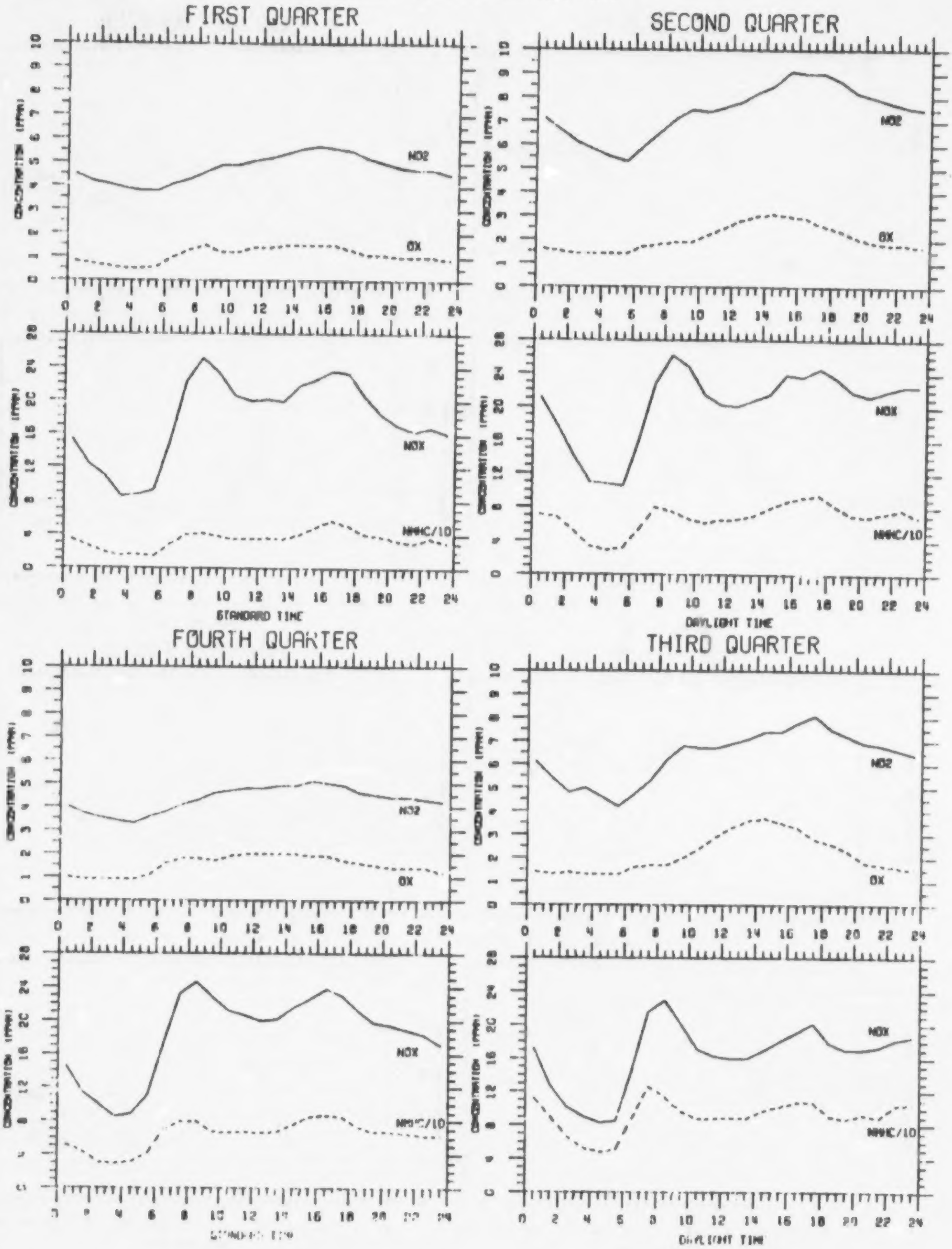


Figure 9.10 Diurnal Patterns at Chicago (1969-1973)

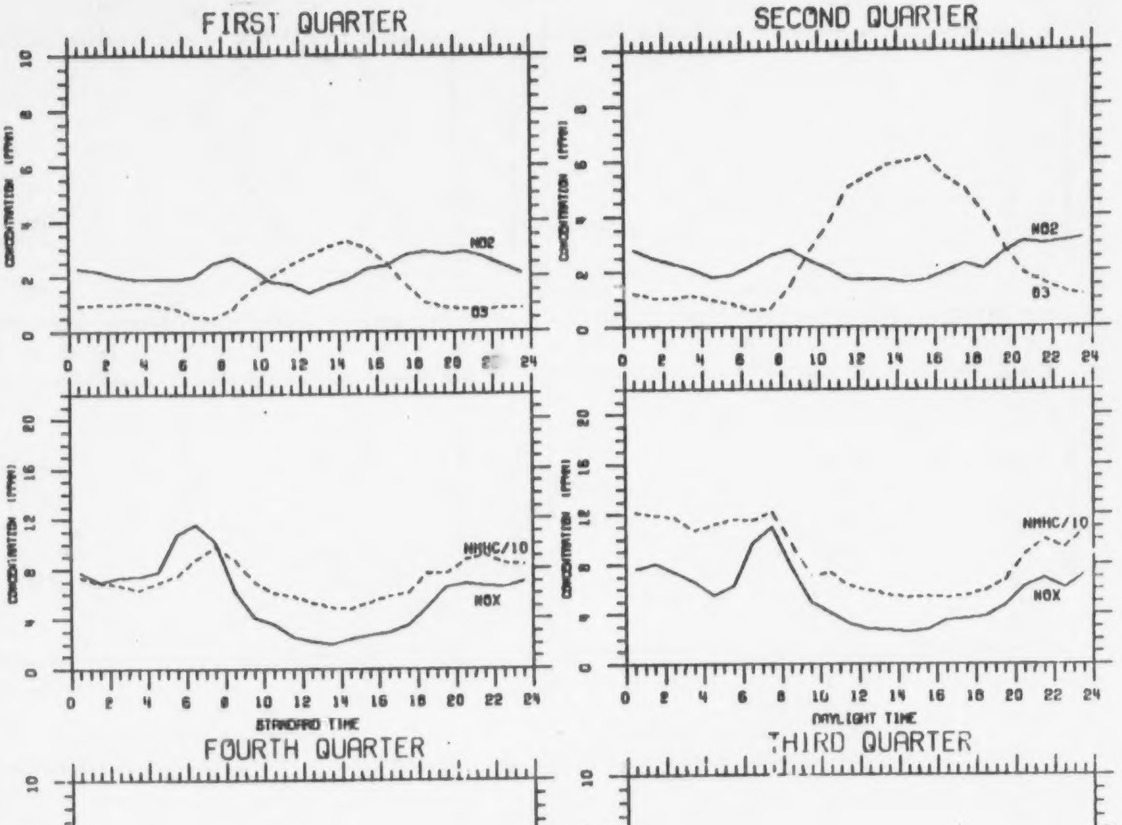
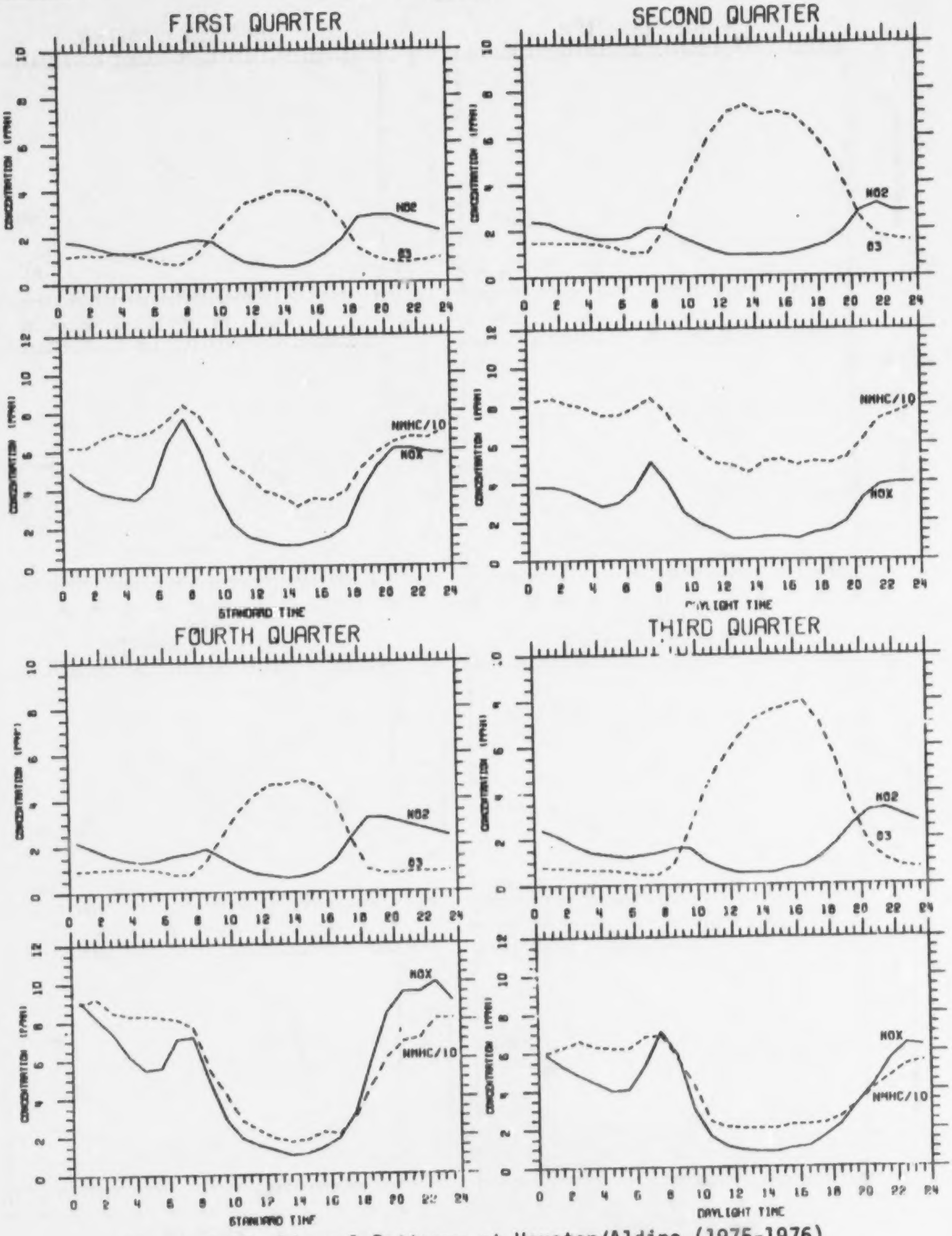


Figure 9.11 Diurnal Patterns at Houston/Mae (1975-1976)



FIRST QUARTER

SECOND QUARTER

FOURTH QUARTER

THIRD QUARTER

Figure 9.12 Diurnal Patterns at Houston/Aldine (1975-1976)

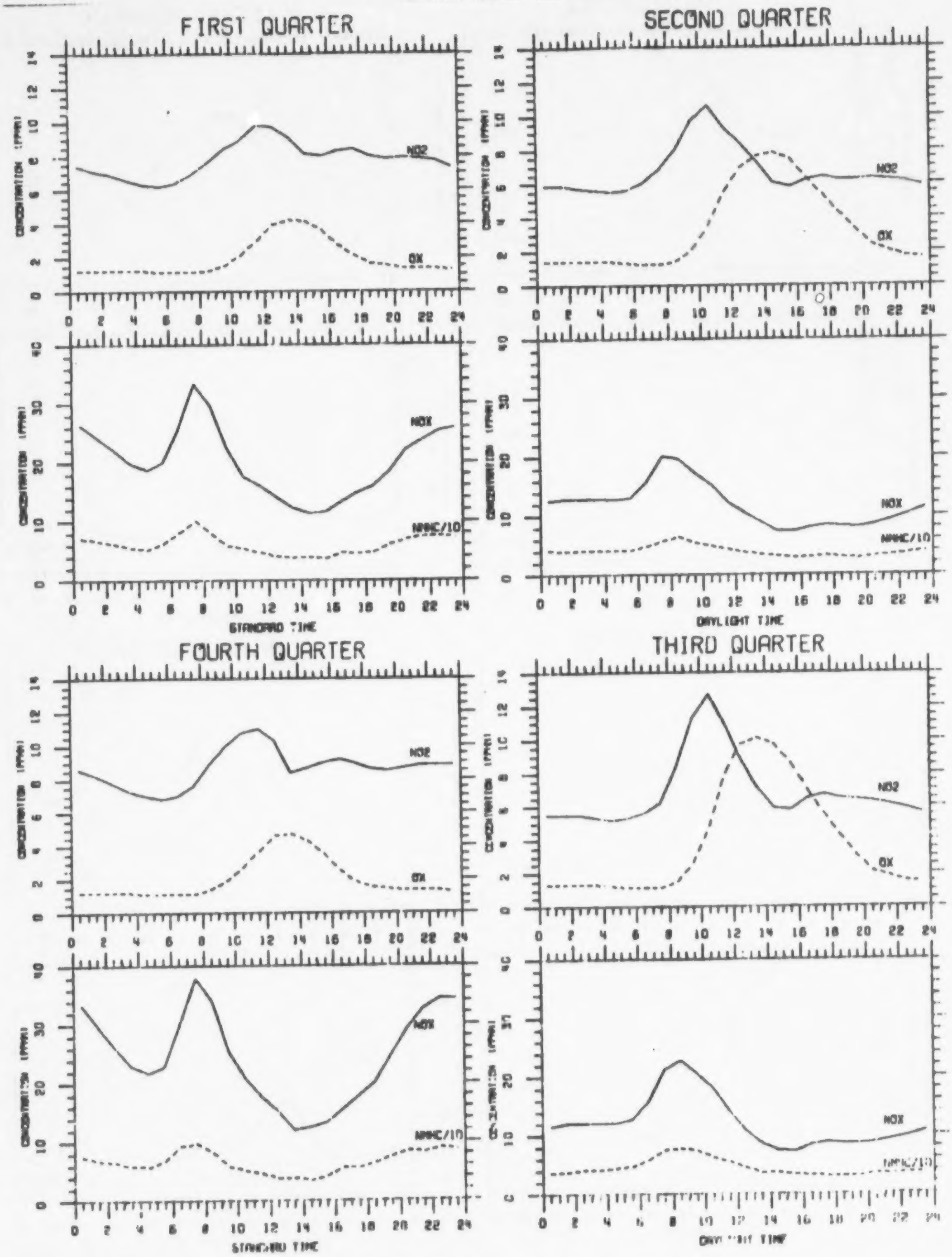


Figure 9.13 Diurnal Patterns at Downtown Los Angeles (1969-1974)

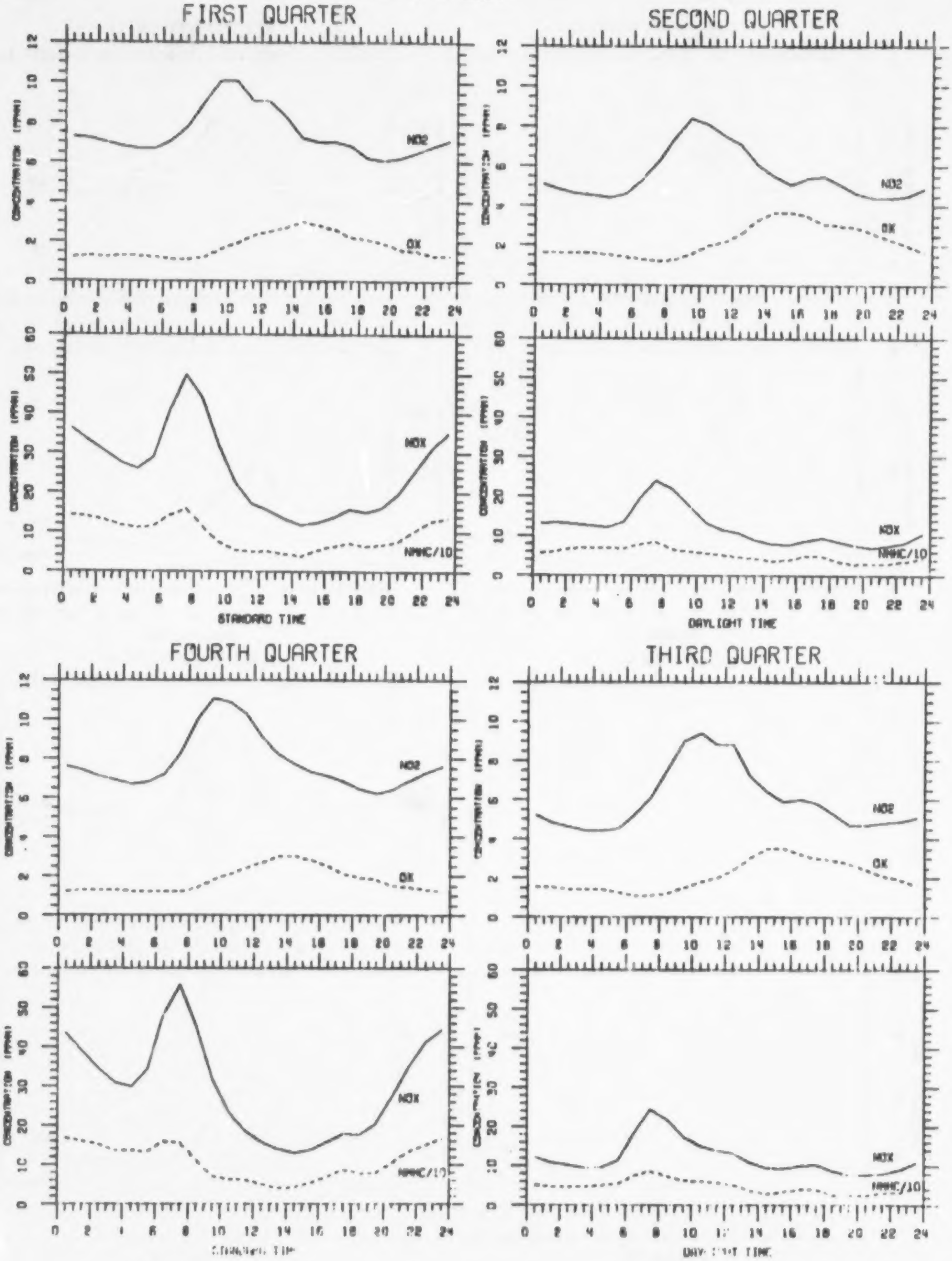


Figure 9.14 Diurnal Patterns at Lennox (1969-1974)

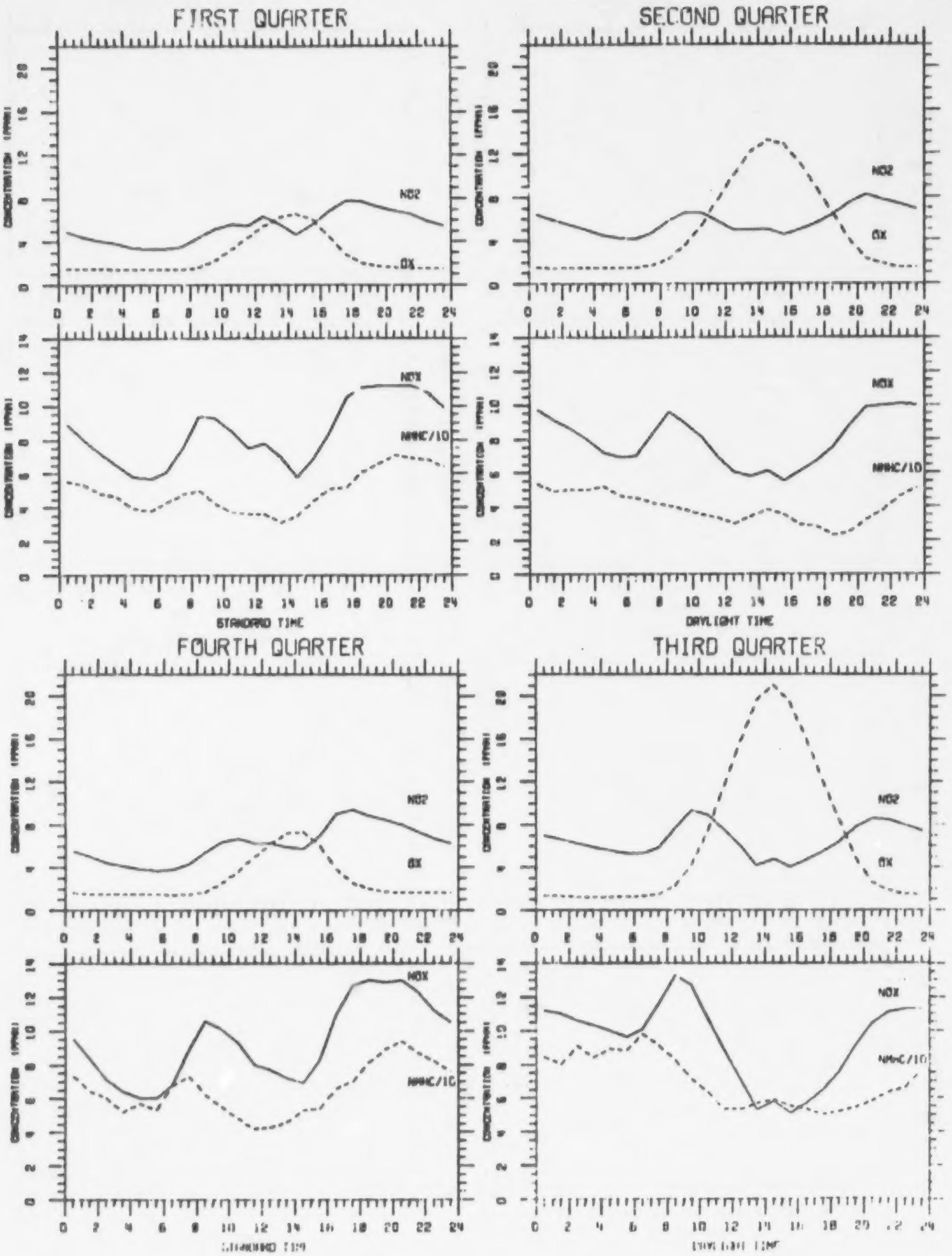


Figure 9.15 Diurnal Patterns at Azusa (1969-1974)

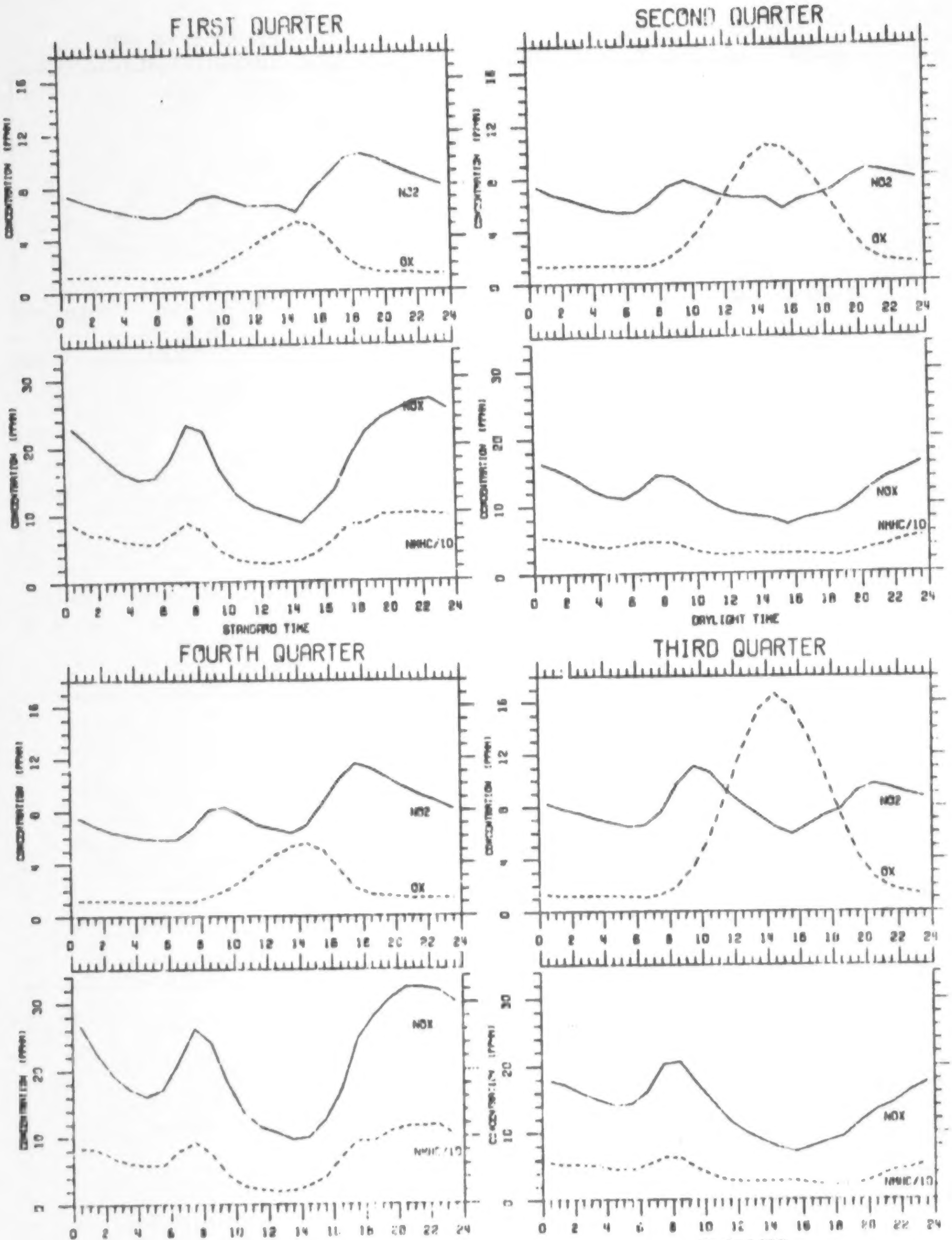


Figure 9.16 Diurnal Patterns at Pomona (1969-1974)

The diurnal patterns for the primary contaminants are similar during the 1st and 4th quarters, and during the 2nd and 3rd quarters. The two winter quarters tend to have stronger nighttime NO_x and NMHC peaks than the two summer quarters, especially in the case of the Los Angeles sites. This reflects stronger nocturnal inversions during the winter.

At all sites and during all quarters, oxidant reaches maximal concentrations in the afternoon. The oxidant peak tends to occur around 1:30 P.M. at Denver, Chicago, Los Angeles, and Lennox and slightly later, around 2:30-3:30 P.M. at the 2 Houston sites and 2 downwind Los Angeles sites (Azusa and Pomona). The 2nd and 3rd quarters are distinguished by higher oxidant levels than the 1st and 4th quarters.

With respect to diurnal patterns for nitrogen dioxide, at each site the 1st quarter is similar to the 4th quarter, while the 2nd quarter is similar to the 3rd quarter. At Denver, the winter quarters show two nearly equal NO_2 peaks, one at 9:30 A.M. and one at 5:30 P.M. In the summer, NO_2 peaks are lower at Denver, and the nighttime maximum occurs later (at about 10:30 P.M.). Chicago shows very little diurnal variation in NO_2 concentrations during the winter, although a single, minor peak is evident at about 4:30 P.M. NO_2 concentrations are higher during the summer in Chicago, and the peak at 4:30 P.M. is much more pronounced.

At Houston Mae, the winter quarters exhibit two nearly equal NO_2 peaks, one at 8:30 A.M. and one at 6:30 P.M. The evening NO_2 peak occurs later (about 11:30 P.M.) during the summer at Houston/Mae. Houston/Aldine shows a pronounced nighttime NO_2 peak, about 6:30 P.M. in the winter and 9:30 P.M. in the summer.

The summer NO_2 maximum is nearly the same as the winter NO_2 maximum at both Houston sites.

Los Angeles and Lennox exhibit a single major peak in NO_2 at about 10:30 A.M. during all seasons. At Los Angeles, the morning peak in the summer quarters exceeds the morning peak in the winter quarters. At Lennox, the morning peak is higher in winter than in summer. The downwind Los Angeles sites (Azusa and Pomona), show two NO_2 peaks during the day, one in the morning (at about 9:30 A.M.) and one in the evening. In the winter, the evening peak occurs around 6:30 P.M. and is larger than the morning peak. In the summer, the evening peak occurs around 9:30 P.M. at a level close to that of the morning peak. The summer maxima in Azusa and Pomona have about the same strength as the winter maxima.

The above observations indicate that diurnal patterns for each pollutant are similar in the 1st and 4th quarters, and in the 2nd and 3rd quarters. This suggests that multiple seasonal divisions, according to individual quarters of the year, are not necessary. A single seasonal division (summer vs. winter) appears adequate for the empirical modeling study.

The diurnal patterns also suggest averaging times for the variables to be included in the empirical models. The dependent variable, nitrogen dioxide, usually reaches two minima at around 5:30 A.M. and 3:30 P.M. Thus, it appears appropriate to select 6:00 A.M. to 4:00 P.M. for "daytime average" NO_2 and 4:00 P.M. to 6:00 A.M. for "nighttime average" NO_2. The daytime peak NO_2 will be taken as the peak hour between 6:00 A.M. and 2:00 P.M., while the nighttime peak NO_2 will be the peak hour between 4:00 P.M. and 2:00 A.M. The only exception to these rules is Chicago, which attains a single NO_2 peak in the late afternoon. For consistency with other sites, the daytime and nighttime averages will be defined the same in Chicago as elsewhere. However, the daytime NO_2 peak will be taken as the peak hour from 6:00 A.M. to 4:00 P.M. in Chicago.

The early-morning precursor levels might best be taken at the time of maximal precursor concentrations, say 7:00 A.M. to 9:00 A.M. However, for consistency with the convention established by other researchers[1,2,3,4], a 6:00 A.M. to 9:00 A.M. average will be used for morning precursors, NO_x and NMHC (or HC).

An average from 4:00 P.M. to 7:00 P.M. will be used to measure evening NO_x as a precursor of nighttime NO_2. In Denver and Chicago, this is the period of the evening maximum in NO_x concentrations. For the Houston and Los Angeles sites, the evening NO_x maximum occurs much later. However, it seems best to use the 4:00 P.M. to 7:00 P.M. average for the Houston and Los Angeles sites as well since this average is a measure of precursor levels at the beginning of the nighttime period. In the empirical models, day-to-day fluctuations in precursors, rather than overall precursor levels, are the key to obtaining the desired relationship. Thus, it is not mandatory that the precursors be measured during the period when they reach a maximum.

Afternoon ozone will also be considered as a precursor to nighttime NO_2. The averaging time for oxidant will be taken as 2:00 P.M. to 4:00 P.M.

The above selections of averaging times for the dependent and independent variables are somewhat arbitrary. Alternative arguments can be made which would suggest different seasonal breakdowns and different averaging times than the ones we have chosen. In our selections, we have attempted to strike a balance between the need for detail to represent a varied and complex phenomenon, and the need for simplicity to facilitate application of the empirical modeling techniques.

9.3 COMPUTER FILE OF DEPENDENT AND INDEPENDENT VARIABLES

To facilitate the empirical modeling analysis, computer files were created which listed, for each site, the values of the dependent and independent variables. Separate files were established for summer (April-September) and winter (October-March). The variables in the files are summarized in Table 9.1. As indicated in Table 9.1, "initial conditions" for NO_2 at the beginning of each daytime and nighttime period were included in the files. These initial conditions, as well as the "precursor variables," might be important in explaining peak and average NO_2 concentrations.

A special computer file was created for Downtown Los Angeles. This file includes seven weather parameters as well as the pollutant variables. The seven meteorological parameters are:

- calculated maximum mixing height for the day (HM);
- maximum temperature for the day (TM);
- minimum relative humidity from 6:00 to 9:00 (RH);
- average wind speed from 9:00 to 12:00 (WS);
- accumulated solar radiation from 7:00 to 12:00 (SR);
- pressure gradient from LAX to Palmdale (PG); and
- temperature gradient from LAX to Palmdale (TG).

Another variable, 6:00-9:00 A.M. carbon monoxide concentration, was also added to the Downtown Los Angeles file. This variable, which is not a causal precursor of NO_2, should be useful for assessing how the intercorrelations between morning precursors affect the statistical results.

Table 9.1 Variables for the Empirical Modeling Analysis

Dependent Variables	Independent Variables	Initial Conditions
	DAYTIME ANALYSIS	
Peak One-Hour NO_2 (from 6:00 A.M. to 2:00 P.M.)* Average NO_2 (6:00 A.M.-4:00 P.M.)	Morning NO_x (6:00 A.M.-9:00 A.M. average) Morning NMHC (6:00 A.M.-9:00 A.M. average) Morning HC (6:00 A.M.-9:00 A.M. average) Six Weather Variables (Downtown Los Angeles only)	Early-Morning NO_2 (5:00 A.M.-6:00 A.M. average)
	NIGHTTIME ANALYSIS	
Peak One-Hour NO_2 (from 4:00 P.M. to 2:00 A.M.) Average NO_2 (4:00 P.M.-6:00 A.M.)	Evening NO_x (4:00 P.M.-7:00 P.M. average) Afternoon O_3** (2:00 P.M.-4:00 P.M. average)	Afternoon NO_2 (3:00 P.M.-4:00 P.M. average)

*For Chicago, this period is 6:00 A.M. to 4:00 P.M.

**CAMP oxidant data were obtained already corrected for interferences. Los Angeles oxidant data were adjusted for interference in this study to represent O_3.

9.4 REFERENCES

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2. J. R. Kinosian and J. Paskind, "Hydrocarbons, Oxides of Nitrogen, and Oxidant Trends in the South Coast Air Basin, 1963-1972," California Air Resources Board--Division of Technical Services, Internal Working Paper.

3. J. C. Trijonis, "Economic Air Pollution Control Model for Los Angeles County in 1975," Environmental Science and Technology, Vol. 8, p. 811, 1974.

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10.0 EMPIRICAL MODELS APPLIED TO DOWNTOWN LOS ANGELES

Before performing empirical studies for all six cities, it is useful to conduct an exploratory analysis with the detailed data base for Downtown Los Angeles. This exploratory analysis should point out the most important variables and should indicate the most promising statistical modeling techniques. Since meteorological data are available for Downtown Los Angeles, the effect of including weather variables in the empirical models can also be investigated. It is important to include meteorology, if possible, to avoid spurious NO_2/precursor relationships which could result if the precursors were correlated with weather factors that govern NO_2 production.

Section 10.1 describes the various statistical techniques that are used to investigate the data from Downtown Los Angeles. Since all these techniques are applied to the same data base, they all yield similar qualitative conclusions concerning the NO_2/precursor dependence. The qualitative conclusions concerning daytime NO_2 are presented in Section 10.2. Included are discussions of the role of NO_x, the importance of initial conditions (e.g., 5:00 A.M. NO_2), the apparent role of hydrocarbons, and the effect including weather parameters. Section 10.3 presents conclusions concerning nighttime NO_2.

Passing from qualitative conclusions concerning the NO_2/precursor dependence to a quantitative model that can be used to predict the impact of precursor control is a difficult and tenuous step. The limitations of our particular approach (see Section 7.2.4 and Section 10.2.4) imply that there will be some uncertainty in the quantitative predictions. Section 10.3 does formulate a predictive model, but this model should at present be regarded as an educated hypothesis that explains certain observed phenomena rather than a definitive tool. The model should be checked by quantitative comparisons with smog-chamber results and with historical air quality trends before full confidence can be placed in it. Such comparisons will be conducted in later chapters of this report.

10.1 STATISTICAL TECHNIQUES FOR EMPIRICAL MODELING

This section discusses some of the statistical techniques that were used to investigate the Downtown Los Angeles data base. The discussion does not delve into the statistical theory behind the methods. Rather, the intent is to provide a brief description of the techniques and to familiarize the reader with the type of outputs available to us.

Graphical Technique Using Mid-Means

In order to provide graphical illustrations of the relationship between a "dependent" variable and an "independent" variable, a program was developed based on a "moving mid-mean" technique. The solid line in Figure 10.1a or 10.1b illustrates the output from this program. In this case, the independent variable is 6-9 A.M. NO_x (NOX69); the dependent variable is daytime peak one-hour NO_2 ($DPKNO_2$). The plotted values for NOX69 represent the average of 30 daily measurements for NOX69, while the plotted values of $DPKNO_2$ represent mid-means[*] of corresponding measurements for $DPKNO_2$. A "moving-window" technique is used which examines the data according to ascending order of NOX69. The window (containing 30 data points) is moved 10 data points to generate each point on the graph.[**] The mid-mean of the dependent variable ($DPKNO_2$) is plotted against the mean of the 30 data points for the independent variable (NOX69).

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[*] The mid-mean is the average of all values between the 25th and 75th percentile.

[**] In some cases with small amounts of data, the window is moved only 5 data points in each step.

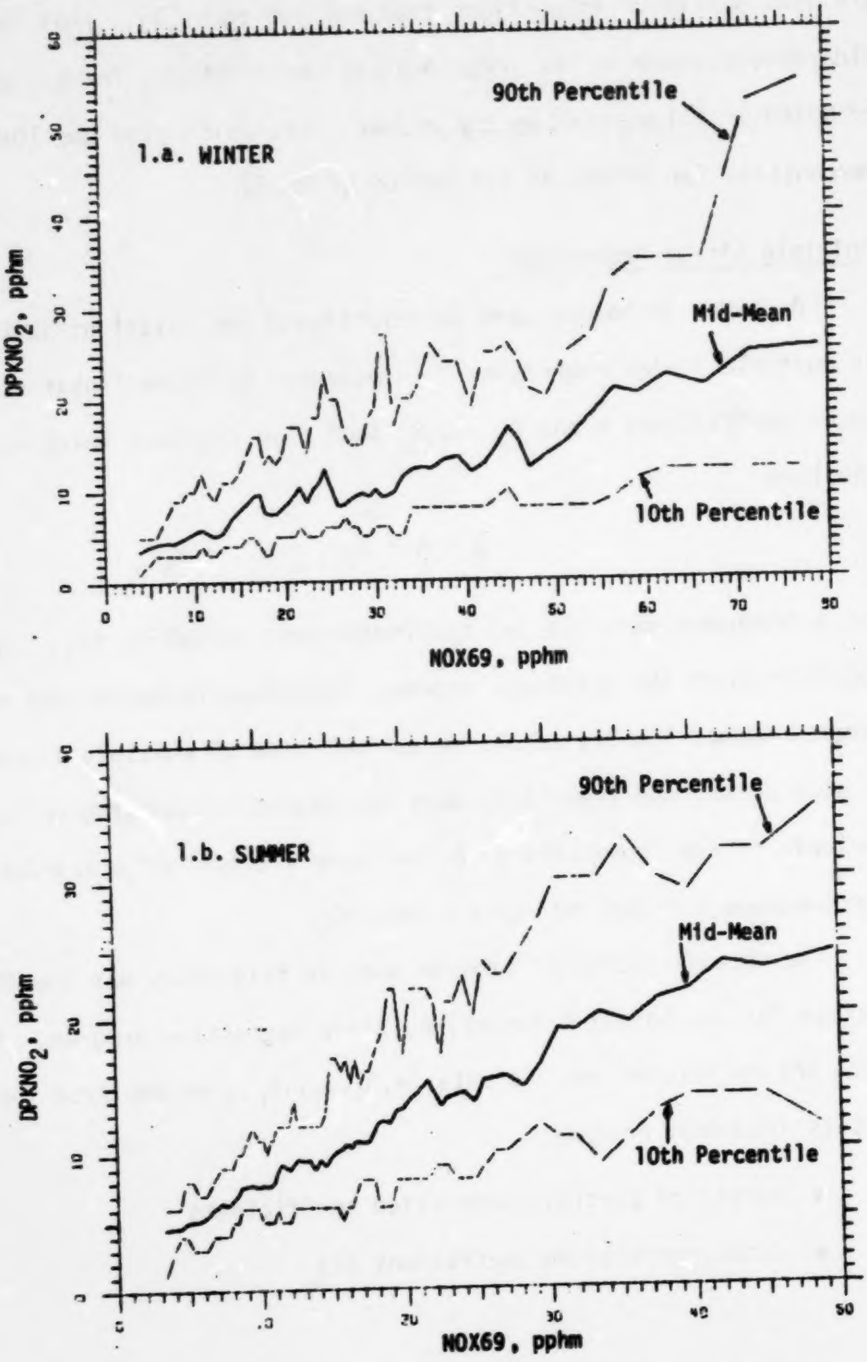


Figure 10.1 Mid-Mean and Percentiles of Daytime Peak NO_2 vs. 6-9 A.M. NO_x

Mid-means are used for the independent variable ($DPKNO_2$) because they are less sensitive to outliers than are averages [1]. That there is considerable scatter in the individual values of $DPKNO_2$ for any given level of NOX69 is illustrated by the dashed lines which give the 10th and 90th percentiles for $DPKNO_2$ as a function of NOX69.

Multiple Linear Regression

A common technique used to investigate the relationship between variables is multiple linear regression. In essence, multiple linear regression computes coefficients A and $B_1,\ldots,B_n$ that give the best least-squares fit of the form

$$y = A + B_1x_1 + \ldots + B_nx_n \qquad (8)$$

for a dependent variable (y) and independent variables ($x_1,\ldots,x_n$). Since application of the graphical mid-mean technique revealed that many dependencies appear linear, extensive use was made of multiple linear regression. In some cases, nonlinearities were introduced by choosing an independent variable in the regression as a nonlinear function of precursor variables, for instance $x = NMHC \cdot NO_x$ or $x = NMHC/NO_x$.

The specific computer program used in this study was the SPSS (Statistical Package for the Social Sciences) multiple regression program. As well as using the regression coefficients ($A,B_1,\ldots,B_n$), we employed the following outputs from that program:

- matrix of partial correlation coefficients
- total correlation coefficient (R)

- percentage of variance explained in the dependent variable (R^2)
- standard error in the regression coefficients
- F-statistic
- residuals of the regression ($y_{actual} - y_{predicted}$).

Multiple Logarithmic Regression

In some cases, multiplicative rather than additive relationships were explored. This was done by performing a linear regression of the form

$$\ell ny = \ell nA + B_1 \ell nx_1 + \ldots + B_n \ell nx_n$$

or

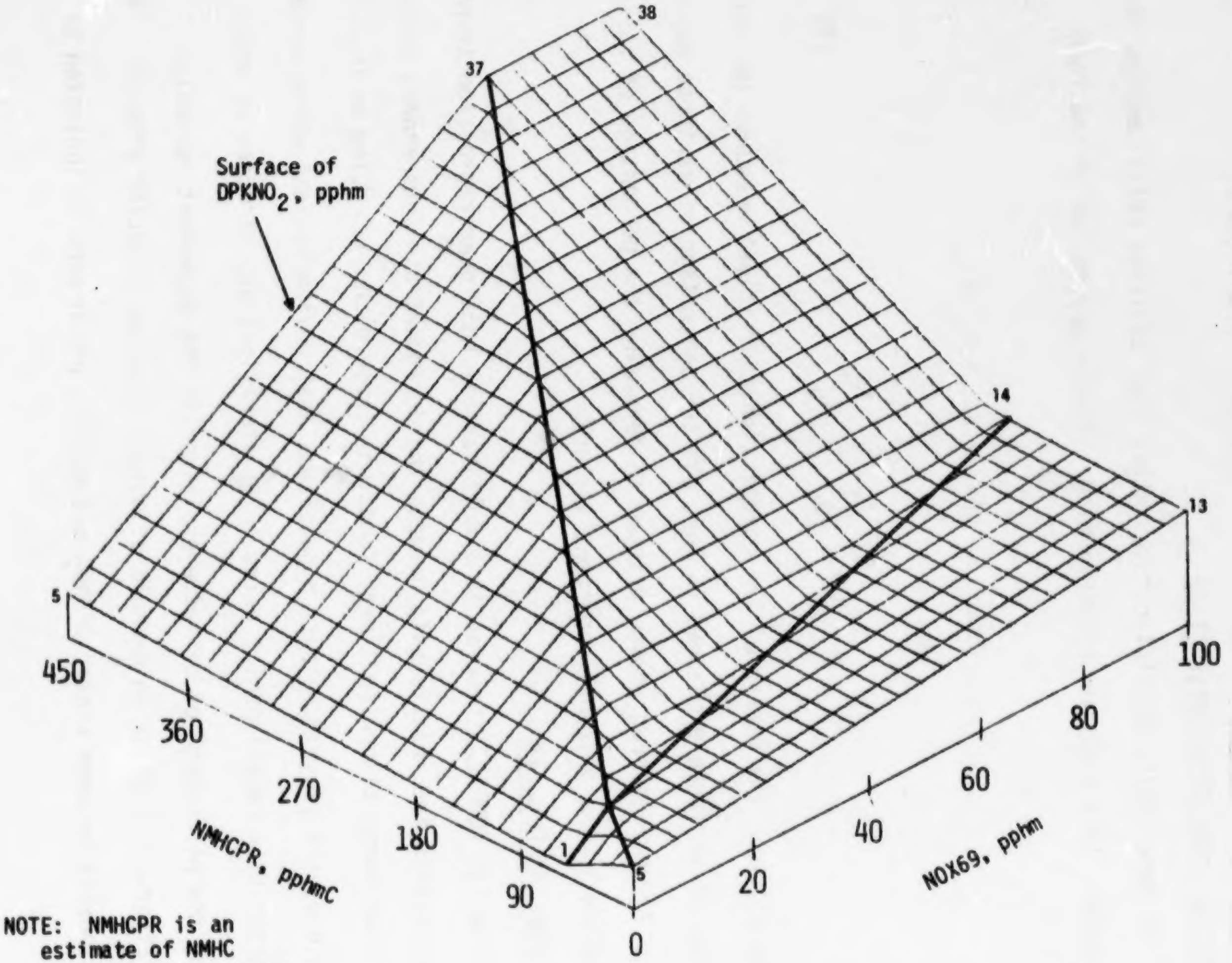
$$y = A x_1^{B_1} x_2^{B_2} \ldots x_n^{B_n} \quad . \qquad (9)$$

In such cases, the square of the correlation coefficient measures the percentage of variance explained in ℓny, not the percentage of variance explained in y. A separate program was written to determine the percentage of variance explained in the original dependent variable.

TSC COMPLIAR Program

The TSC COMPILAR program is a multivariate nonlinear regression technique. It represents the relationship between the dependent and independent variables with continuous piecewise linear functions (hyperplanes). Using an iterative technique, the program selects hyperplanes that define regions where certain characteristic relationships exist. The iterations are directed at maximizing the percentage of variance explained in the dependent variable.

Figure 10.2 gives an example of output from the COMPLIAR program. The relationship between winter $DPKNO_2$ and morning precursors is indicated by



NOTE: NMHCPR is an estimate of NMHC calculated from total hydrocarbon measurements.

Figure 10.2 Output of COMPLIAR Program for $DPKNO_2$ vs. NMHCPR and NOX69, Winter Season

four hyperplanes. This particular example is interesting because it represents the particular case (winter season and peak NO_2) where the most significant hydrocarbon dependence was found. For high values of NO_x (or, more appropriately, for low NMHC/NO_x ratios), winter DPKNO$_2$ appears to be quite sensitive to hydrocarbons.

In this study, we used the COMPLIAR program to obtain a qualitative picture of the relationships in the data and to check the conclusions yielded by other techniques. The predictive models for assessing control strategies were based on simpler regression forms.

10.2 DEPENDENCE OF DAYTIME NO_2 ON PRECURSORS

This section discusses conclusions concerning the daytime NO_2/precursor relationship at Downtown Los Angeles. These conclusions are based on statistical analyses involving the variables listed in Table 10.1, which serves as a glossary for this discussion. All four statistical techniques described in the previous section were used to explore the data. These techniques were employed with various combinations of the variables and with various functional forms.

Since each statistical technique was applied to the same data base, each yielded the same qualitative conclusions concerning the NO_2/precursor dependence. The qualitative aspects of the findings will be the subject of this section. The final section of this chapter will use a specific statistical technique to arrive at a quantitative model.

The relationship between daytime NO_2 and precursors turned out to be very complex. For instance, the effect of hydrocarbons was different on average NO_2 than peak NO_2; was dependent on the season; and was different for high NO_x levels than for low NO_x levels. The observed dependence on hydrocarbons was also sensitive to including weather factors in the analysis. Because of this complexity and because of the large number of variables involved, the investigation of the data was an iterative learning process. It is impractical to describe all of the specific analyses that

Table 10.1 Glossary of Variables for the Daytime Analysis
(All Hours are in Civil Time)

Dependent Variables	
DPKNO$_2$	Peak one-hour NO$_2$ from 6:00 A.M. to 2:00 P.M. in pphm
DAVNO$_2$	Average NO$_2$ from 6:00 A.M. to 4:00 P.M. in pphm
Independent Variables (Pollutants)	
NOX69	6:00-9:00 A.M. average NO$_x$ concentration in pphm
NO$_2$5	4:00-5:00 A.M. NO$_2$ concentration in pphm (if the 4:00-5:00 A.M. reading was missing, 3:00-4:00 A.M. or 2:00-3:00 A.M. was used)
INTNO	NOX69-NO$_2$5, representing overnight NO plus morning injection of NO
NMHC69	6:00-9:00 A.M. nonmethane hydrocarbon concentration in pphmC
HC69	6:00-9:00 A.M. total hydrocarbon concentration in pphmC
NMHCPR	(HC69-100)/2, approximate value of NMHC calculated from total HC concentration
CO69	6:00-9:00 A.M. CO concentration
Independent Variables (Meteorology)	
HM	calculated daily maximum mixing height
TM	maximum daily temperature
RH	minimum relative humidity (6:00 A.M.-7:00 P.M.)
WS	average wind speed (9:00-12:00 A.M.)
SR	accumulated solar radiation (7:00-12:00 A.M.)
PG	pressure gradient from LAX to Palmdale
TG	temperature gradient from LAX to Palmdale

were performed. What follows is a selected sample of results that best illustrates the relationships, and lack of relationships, that exist in the data.

10.2.1 Morning Precursor Variables

The original intent in the empirical modeling study was to use NOX69 and NMHC69 as the morning precursor variables for daytime NO_2. There was some concern, however, about the accuracy of the NMHC data. NMHC values are obtained by subtracting methane (CH_4) measurements from total hydrocarbon (HC) measurements. A recent study indicates that methane and total hydrocarbon data tend to be of uncertain reliability [2]. NMHC values, obtained by subtracting one uncertain measurement from another one of comparable magnitude, are especially suspect. A further problem in the case of Los Angeles NMHC data is round-off error. HC and CH_4 are both reported only to the nearest ppm. Thus, an individual hourly NMHC measurement can only assume values of 0, 100 pphm, 200 pphm, etc. This is an extremely gross resolution considering that average NMHC concentrations in Los Angeles are less than 100 pphm.

Because of the concern about the NMHC data, total hydrocarbons (HC69) were also included in the data base. If the NMHC data proved of little use, it might be possible to conduct the analysis with the total hydrocarbon measurements.

Another concern was the colinearity problem with morning precursor variables. The intercorrelations between the precursors might make it difficult to separate out the individual effects of NMHC and NO_x on daytime NO_2. To assess this problem, CO69 was included in the data base. This variable bears no causal relationship to NO_2, and it is interesting to determine if the statistical techniques can find that result.

Table 10.2 illustrates the correlation coefficients between the morning precursor variables (NOX69, NMHC69, HC69, and CO69). As expected, high intercorrelations exist between the 6:00-9:00 A.M. concentrations because the pollutants tend to rise and fall together, depending on dispersive conditions. It is notable that the smallest correlations occur when NMHC is one of the variables. As previously remarked, the NMHC data are considered the least reliable.

As a test of the relative importance of the variables as NO_2 precursors, logarithmic regressions were conducted between daytime NO_2 (both peak and average) and pairs of the precursor variables. For example, the regression for $DPKNO_2$ vs. NOX69 and NMHC69 was of the form

$$\ell n\, DPKNO_2 = \ell n A + B_1\, \ell n NOX69 + B_2\, \ell n NMHC69$$

$$\text{or} \qquad DPKNO_2 = A \cdot NOX69^{B_1} \cdot NMHC69^{B_2} \quad . \qquad (10)$$

Table 10.3 lists the regression coefficients (B_1 and B_2) for each pair of independent variables.

Table 10.3 reveals that the coefficient for NOX69 tends to dwarf the coefficient for any other variable paired with it. In particular, CO69 tends to be assigned insignificant importance when it is paired with NOX69, even though CO69 is the morning pollutant variable most highly correlated with NOX69 (see Table 10.2). The dominance of NOX69 is not surprising; we expect daytime NO_2 to be most strongly dependent on NOX69. Part of NOX69

Table 10.2 Correlation Coefficients Between Morning Precursor Variables

Summer

	NOX69	HC69	NMHC69	CO69
NOX69	1.00	0.78	0.65	0.79
HC69		1.00	0.78	0.77
NMHC			1.00	0.66
CO69				1.00

Winter

	NOX69	HC69	NMHC69	CO69
NOX69	1.00	0.81	0.74	0.86
HC69		1.00	0.81	0.81
NMHC69			1.00	0.79
CO69				1.00

Table 10.3 Logarithmic Regression Coefficients for Pairs of Morning Pollutant Variables

	Summer				Winter			
	NOX69	HC69*	NMHC69	CO69	NOX69	HC69*	NMHC69	CO69
Day	0.68**	0.05			0.50**	0.25**		
Peak	0.68**		0.03		0.63**		0.04	
NO_2	0.67**			0.06	0.67**			0.15
		0.44**	0.12**			0.61**	0.09**	
		0.26**		0.50**			0.07	0.66**
	NOX69	HC69*	NMHC69	CO69	NOX69	HC69*	NMHC69	CO69
Day	0.63**	-0.01			0.49**	0.19**		
Average	0.63**		-0.01		0.60**		0.02	
NO_2	0.64**			-0.02	0.62**			0.00
		0.38**	0.09**			0.55**	0.08**	
		0.21**		0.43**		0.38**		0.35**
			0.07**	0.50**			0.08**	0.56**

*In the logarithmic regressions, HC69-80 (units are in pphmC) is used to avoid singularities of the logarithm function.

**Coefficients significant from zero at 99% confidence level.

is already NO_2 (which contributes to the daytime peak and average NO_2), while the rest of NOX69 is NO (which is a source of further NO_2). However, it is encouraging that the regression analysis does discover the importance of NO_x. This indicates that the intercorrelations between the variables are not so high as to make the real precursor (NO_x) indistinguishable from the surrogate (CO).

For the regressions in Table 10.3, the percentage of variance explained in $\ell n DPKNO_2$ and $\ell n DAVNO_2$ tended to be around 55% to 65% (R = 0.75 to 0.80) when NOX69 was one of the independent variables.* When NOX69 was not included, the percentage of variance explained dropped to around 30% to 50% (R = 0.55 to 0.70).* This again indicates the particular importance of NOX69 as a precursor variable.

Another interesting feature of Table 10.3 is that HC69 is the only variable which appears to retain some importance when it is paired with NOX69. In the winter, the HC69 coefficients for both peak and average NO_2 are highly significant. The NMHC69 coefficients, on the other hand, are always insignificant when NO_x is included and are small even when NMHC69 is paired with HC69 or CO69. This is a further indication that the NMHC data for Los Angeles are not as useful as the HC data for empirical modeling.

That the dependence of NO_2 on HC69 is not solely due to intercorrelation with NOX69 can be seen by graphing NO_2 vs. morning NO_x, while stratifying for hydrocarbon levels. Such plots (presented later) show that higher HC69 levels tend to yield higher NO_2 concentrations for fixed values of morning NO_x. When similar plots are prepared, stratified by NMHC69, little, if any, hydrocarbon effect is evident. Again, this is probably a reflection of the poorer quality of the NMHC data.

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*The percentage variance explained in the original dependent variables, $DPKNO_2$ and $DAVNO_2$, was slightly less than for the logarithms, typically about 5% to 10% less.

Because of the questions concerning the NMHC data, it was decided to use HC69 instead of NMHC69 as a precursor variable for daytime NO_2. To allow a basis for comparison with other studies using NMHC data, the HC69 were adjusted to be approximately representative of NMHC values. This new variable, denoted by NMHCPR, is defined by the formula*

$$\mathrm{NMHCPR} = \frac{\mathrm{HC69} - 100}{2} \qquad (11)$$

with units in pphmC.

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*A set of field measurements by the California Air Resources Board [3] arrived at a formula,

$$\mathrm{NMHC} = \frac{\mathrm{HC} - 135}{1.55} \; .$$

A regression applied with our data base yields the formula

$$\mathrm{NMHC} = \frac{\mathrm{HC} - 119}{3.22} \; .$$

We chose the constant "100" in Equation (11) to avoid negative values of NMHCPR (the minimum reported value for HC69 is 100). The constant "2" in Equation (11) is somewhat arbitrary; one-digit significance is chosen as an indication of the uncertainty in that constant.

10.2.2 Importance of Initial NO_2

The previous section indicated that NOX69 is an important variable in explaining daytime peak and average NO_2. Part of NOX69 consists of NO_2 leftover from the previous night. This initial NO_2 can be distinguished from the remainder of NOX69, which consists of NO leftover from the night plus the injection of morning NO emissions. Since it already starts out as NO_2, initial NO_2 may have special significance.

To examine the importance of initial NO_2, NOX69 was split into two variables: NO_25, NO_2 at 5:00 A.M., and INTNO, NOX69 - NO_25. Multiple linear regressions were run of the form

$$\underset{\text{(or } DAVNO_2\text{)}}{DPKNO_2} = A + B_1 \cdot NO_25 + B_2 \cdot INTNO \quad . \qquad (12)$$

The results of these regressions are summarized in Table 10.4. The high values for percentage variance explained (R^2) are encouraging. These regressions indicated that both NO_25 and INTNO are highly significant (as measured by the F-statistic). Thus, it seemed important to distinguish initial NO_2 in the empirical modeling analysis.

Most of the regression coefficients (B_1 and B_2) in Table 10.4 make sense physically. Initial NO_2 contributes more to peak NO_2 than to average NO_2, because peak NO_2 occurs early in the daytime period (i.e., closer to the time of the NO_25 measurement). The contribution of INTNO, as measured by B_2, is much greater in summer than winter because photochemistry is more active in summer, leading to a greater conversion of morning NO into NO_2.*

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*The only result in Table 10.4 that seems unreasonable is the fact that the contribution from NO_25 (B_1) for the winter peak exceeds 1.0. However, it is only slightly in excess of unity.

The regressions according to Equation (12) also demonstrate that the constant "A" is substantial. This constant might be considered a measure of the amount of daytime NO_2 that is not relatable to $NO_2 5$ or to INTNO, such as NO_2 resulting from post 9:00 A.M. emissions.

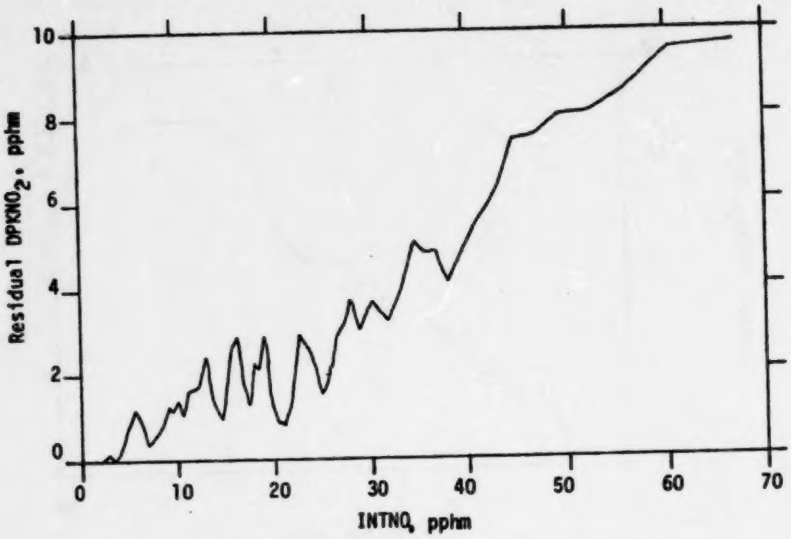
Table 10.4 Values of A, B_1, and B_2 for Regressions According to Equation (12)

	R	R^2	A (Constant Term)	B_1 ($NO_2 5$ Coefficient)	B_2 (INTNO Coefficient)
WINTER					
$DPKNO_2$	0.75	0.57	0.2 pphm	1.18	0.18
$DAVNO_2$	0.83	0.68	0.6 pphm	0.83	0.11
SUMMER					
$DPKNO_2$	0.77	0.60	2.5 pphm	0.78	0.43
$DAVNO_2$	0.80	0.64	2.3 pphm	0.53	0.21

To check whether daytime NO_2 (peak or average) actually depends on INTNO in a linear fashion, the contribution of "nonrelatable" NO_2 (the constant A) and the contribution of initial NO_2 ($B_1 \cdot NO_2 5$) were subtracted from total daytime NO_2 to yield "residual daytime NO_2,"

$$\text{Residual Daytime } NO_2 = \text{Daytime } NO_2 - A - B_1 \cdot NO_2 5. \qquad (13)$$

This was plotted vs. INTNO using the mid-mean graphical technique. The results for winter are shown in Figure 10.3, and for summer; in Figure 10.4. These graphs indicate that the dependence of daytime NO_2 (both peak and average) on INTNO is essentially linear.



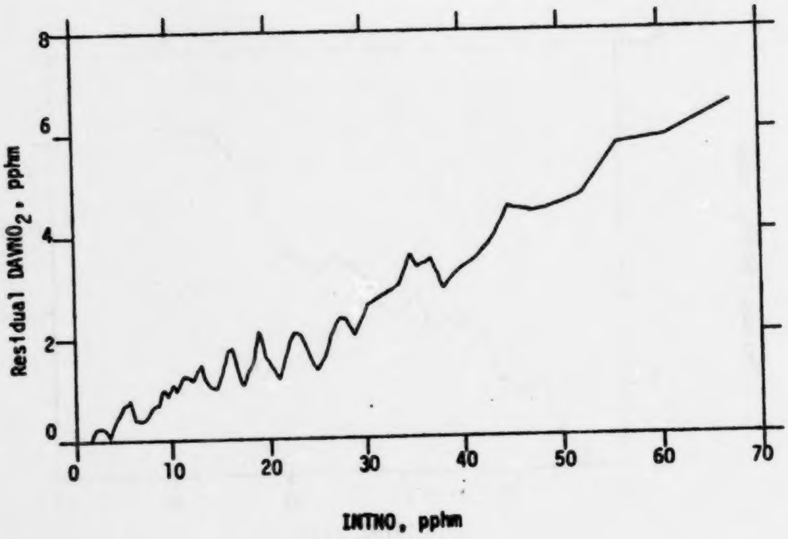


Figure 10.3 Dependence of Residual Daytime NO_2 on INTNO (NOX69 - $NO_2$5), Winter Season

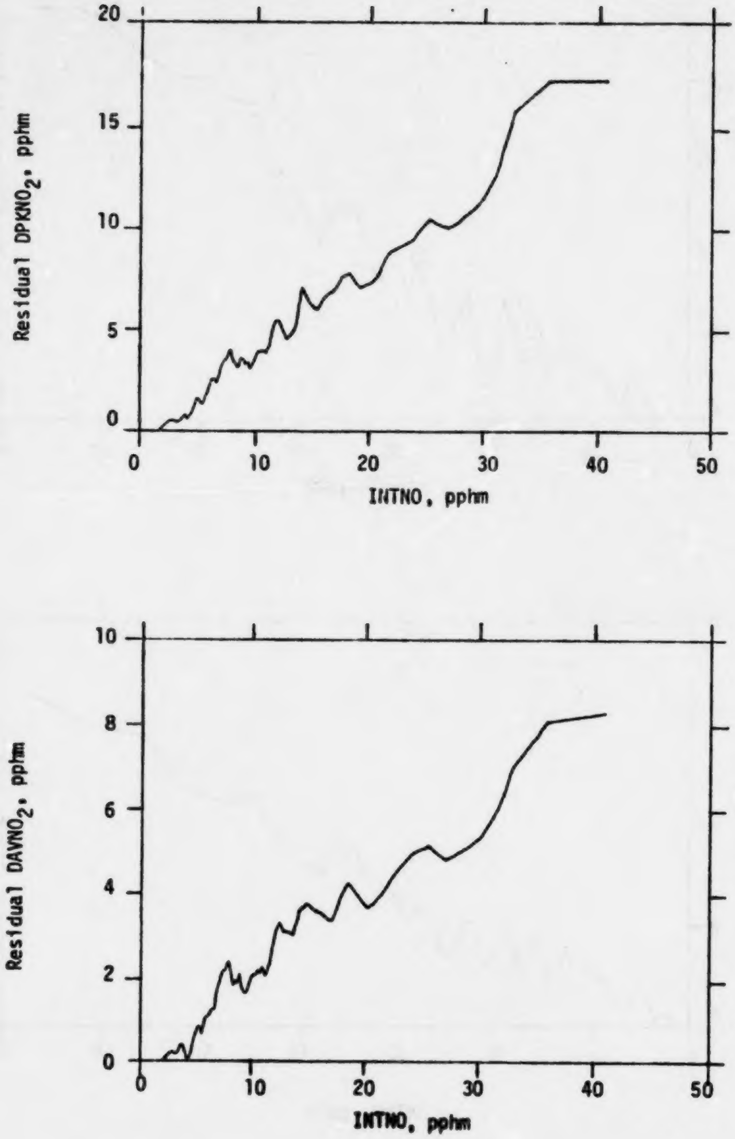


Figure 10.4 Dependence of Residual Daytime NO_2 on INTNO (NOX69 - $NO_2$5), Summer Season

10.2.3 Dependence of Daytime NO_2 on Hydrocarbons

The dependence of daytime NO_2 on hydrocarbons at Downtown Los Angeles was investigated using all four statistical techniques: graphical analysis, linear regression, logarithmic regression, and TSC's COMPLIAR program. These techniques consistently pointed toward several general conclusions:

- For fixed NOX69 (or for fixed INTNO), hydrocarbons appeared to be positively related to peak and average daytime NO_2; i.e., hydrocarbon reductions would tend to decrease both peak and average daytime NO_2. However, the hydrocarbon dependence was of secondary importance compared with the NO_x dependence.
- The hydrocarbon dependence is greater for peak NO_2 than for average NO_2.
- The hydrocarbon effect appears to be greater in winter than in summer.
- The hydrocarbon effect is greater at high NO_x levels (NOX69 $\geq$ 20 pphm) than at low NO_x levels.

Some of these conclusions are illustrated in Table 10.5. Table 10.5 lists the hydrocarbon regression coefficient for logarithmic regressions of daytime NO_2 vs. NOX69 and HC69. The data are split by season and for NOX69 $\leq$ 20 pphm and NOX69 $\geq$ 20 pphm. The regression coefficients for HC are greater for $DPKNO_2$ than for $DAVNO_2$; are higher in winter than in summer; and are negligible for NOX69 < 20 pphm.

Table 10.5 Hydrocarbon Regression Coefficient for Logarithmic Regressions of Daytime NO_2 vs. NOX69 and HC69 *

	NOX69 < 20	NOX69 ≥ 20
WINTER		
DAY PEAK NO_2	0.04	0.61**
DAY AVG. NO_2	0.04	0.45**
SUMMER		
DAY PEAK NO_2	0.01	0.30**
DAY AVG. NO_2	-0.03	0.13**

*Actually, the variable (HC69-80) is used for logarithmic regressions.
**Significant at 95% confidence level.

It is encouraging to note that these results agree qualitatively with recent smog-chamber tests and with expectations based on theoretical arguments. A smog-chamber study of the NO_2/precursor dependence[4] indicated that both peak and average NO_2 were related positively to hydrocarbon input, that the hydrocarbon dependence was secondary compared with the NO_x dependence, and that the effect of hydrocarbons was relatively greater at higher values of initial NO_x. Physical arguments have been advanced that hydrocarbon reductions would decrease peak NO_2 more than average NO_2*[5] and that the hydrocarbon effect should be greater in winter than in summer[6].

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*It has also been argued that (for fixed NO_x) morning hydrocarbons should be negatively correlated with NO_2 levels late in the day. As will be shown later, this effect is also evident in the aerometric data.

For investigating the hydrocarbon dependence quantitatively, it seemed best to use residual daytime NO_2 (as defined by Equation (13) as the dependent variable. The contribution of initial NO_2 and of NO_2 not directly relatable to 6:00-9:00 A.M. precursors would already be subtracted out. We would, in effect, be examining the extra NO_2 brought about by INTNO and NMHCPR.

In Figures 10.5 and 10.6, the effect of hydrocarbons is taken into account by plotting residual NO_2 vs. INTNO, with the data stratified by hydrocarbon (NMHCPR)level. Figure 10.5 is for winter, while Figure 10.6 is for summer. The vertical distance between the curves represents the impact of hydrocarbons on daytime NO_2. These results show graphically some of the conclusions alluded to earlier: The hydrocarbon effect is of secondary importance, is greater for the daytime peak than the daytime average, and is greater in winter than in summer.

An alternative way of examining the effect of hydrocarbons is to use the hydrocarbon-to-NO_x ratio, NMHCPR/NOX69. Figures 10.7 and 10.8 give plots of residual NO_2 vs. INTNO, with the data stratified by the hydrocarbon-to-NO_x ratio. These plots are interesting because they indicate that residual daytime NO_2 may be proportional to INTNO, with the proportionality constant depending on the hydrocarbon-to-NO_x ratio.

Our hypothesis is that morning hydrocarbons (NMHCPR) impact daytime NO_2 by governing the amount of INTNO converted to NO_2. In effect, the constant "B_2" in Equation (12) depends on hydrocarbons. After considerable thought, it was decided that an appropriate way to quantify the

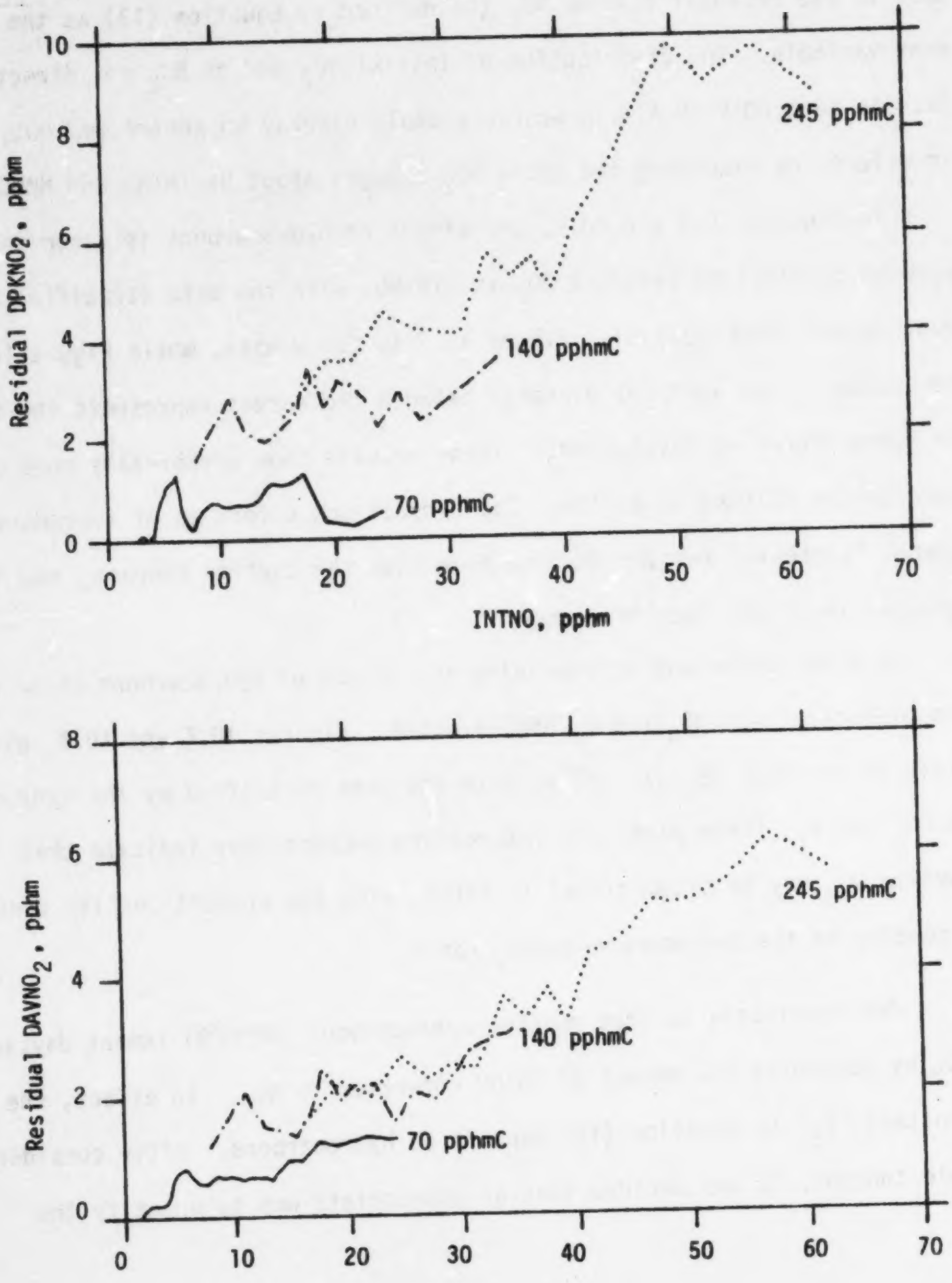
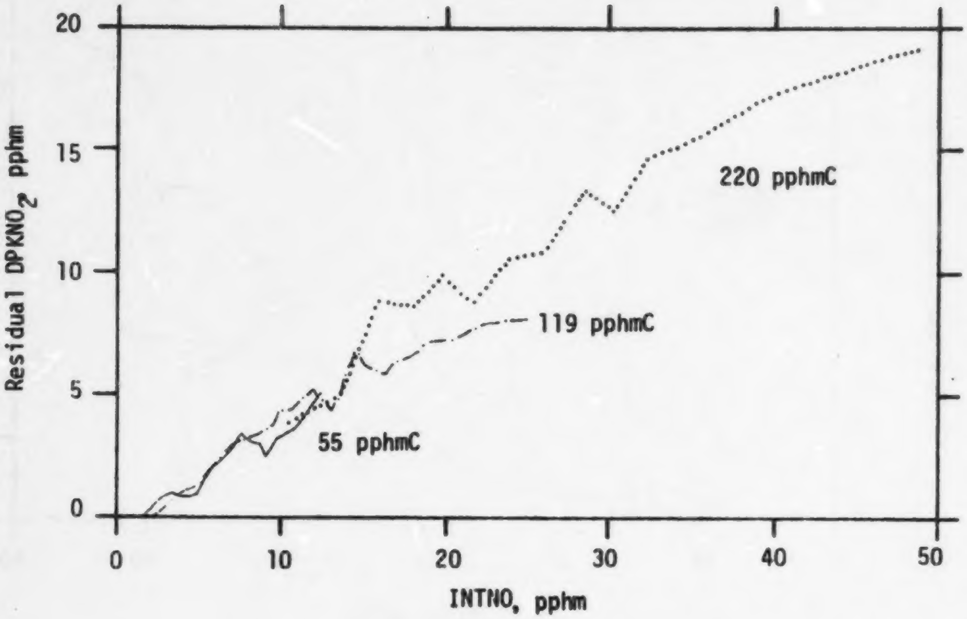


Figure 10.5 Residual Daytime NO$_2$ vs. INTNO at Various Hydrocarbon Levels, Winter Season



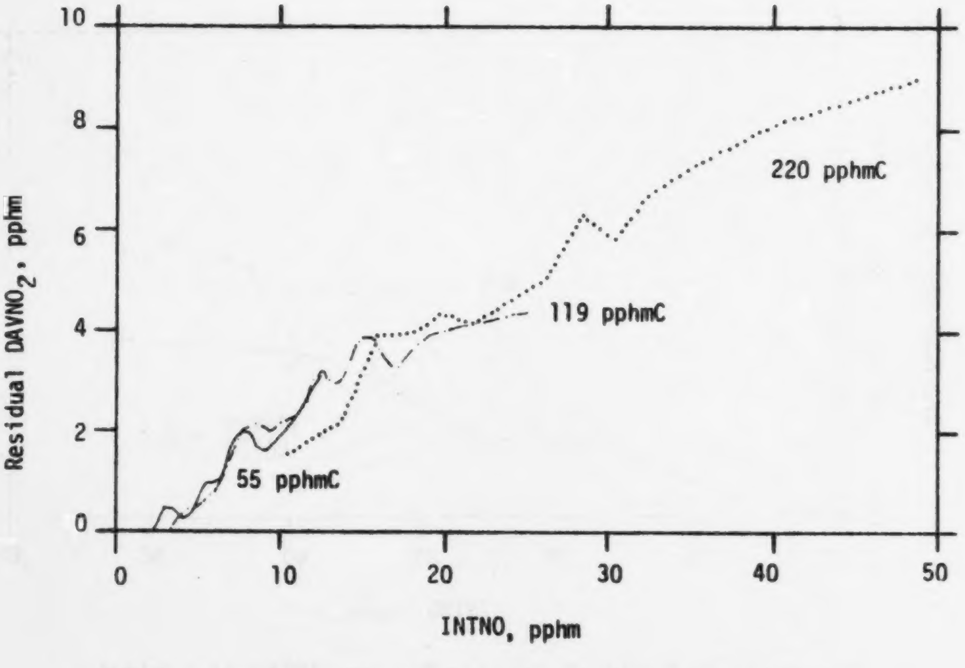
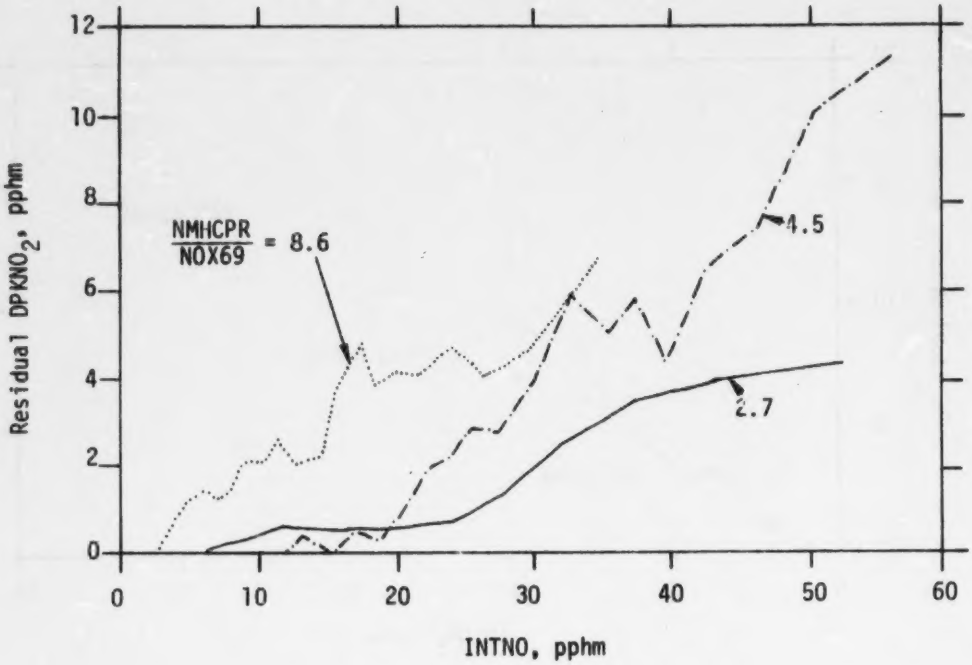


Figure 10.6 Residual Daytime NO_2 vs. INTNO at Various Hydrocarbon Levels, Summer Season



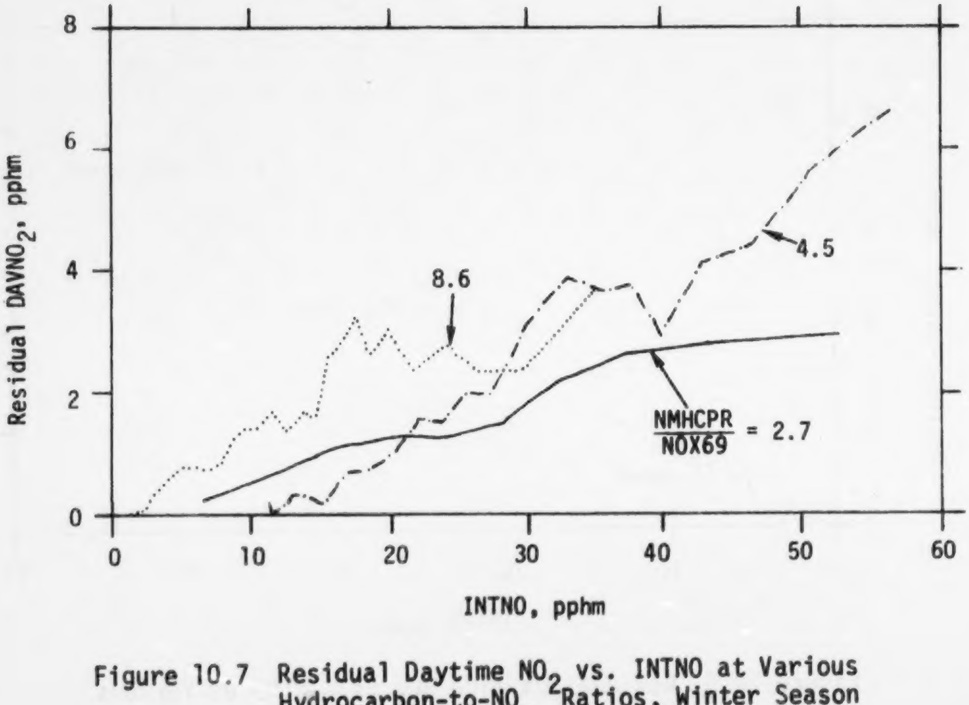
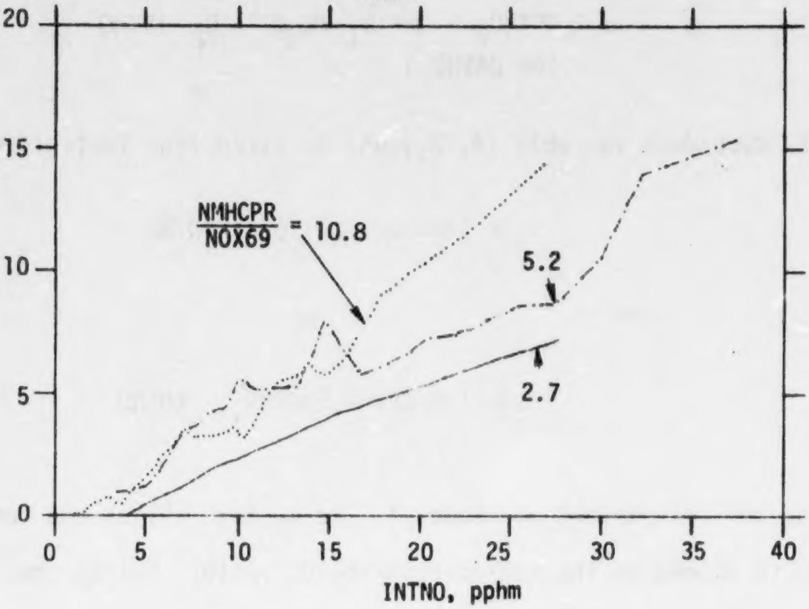


Figure 10.7 Residual Daytime NO_2 vs. INTNO at Various Hydrocarbon-to-NO_x Ratios, Winter Season



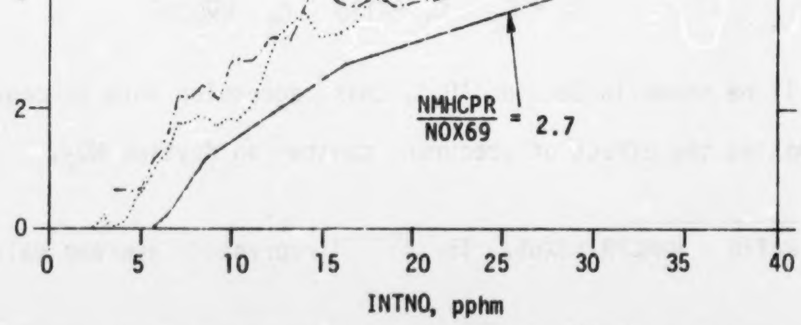


Figure 10.8 Residual Daytime NO_2 vs. INTNO at Various Hydrocarbon-to-NO_x Ratios, Summer Season

hydrocarbon dependence would be to conduct a linear regression,

$$y = C_0 + C_1x_1 + C_2x_2, \qquad (14)$$

with

$$y \equiv \underset{\text{(or DAVNO}_2\text{)}}{\text{DPKNO}_2} - A - B_1 \cdot \text{NO}_2\text{5} - B_2 \cdot \text{INTNO} \qquad (14a)$$

as the dependent variable (A, B_1, and B_2 taken from Table 10.4) and with

$$x_1 \equiv [\text{RATIO} - \overline{\text{RATIO}}] \cdot \text{INTNO} \qquad (14b)$$

and

$$x_2 \equiv [\text{NMHCPR} - \overline{\text{NMHCPR}}] \cdot \text{INTNO} \qquad (14c)$$

as the two independent variables.* The x_1 term allows the conversion of INTNO to depend on the hydrocarbon-to-NO_x ratio. Noting that NMHCPR is just RATIO · NOX69, we can see that the x_2 term allows the effect of RATIO to change with the level of NOX69.

The regression according to Equation (14) will yield a constant term, C_0, and two regression coefficients, C_1 and C_2. The predictive equation for daytime NO_2 would then be

$$\underset{\text{(or DAVNO}_2\text{)}}{\text{DPKNO}_2} = (A + C_0) + B_1 \cdot \text{NO}_2\text{5} + \text{INTNO} \cdot [B_2' + C_1 \cdot \text{RATIO} + C_2 \cdot \text{NMHCPR}] , \qquad (15)$$

where

$$B_2' = B_2 - C_1 \cdot \overline{\text{RATIO}} - C_2 \cdot \overline{\text{NMHCPR}} \quad .$$

As will be shown in Section 10.4, this regression form is convenient for estimating the effect of precursor control on daytime NO_2.

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*RATIO ≡ NMHCPR/NOX69. The "‾‾‾" represents average values.

The reader may note that it would seem equivalent to run linear regression with daytime NO_2 (peak or average) as the dependent variable and with $NO_2$5, INTNO, INTNO · RATIO, and INTNO · NMHCPR as four independent variables. However, the last three of these independent variables are highly intercorrelated (partial correlation coefficient = 0.9) because they all involve the parameter INTNO. Because of this intercorrelation, it would be dangerous to attach physical meanings to the relative sizes of the regression coefficients. In particular, the existence of a real hydrocarbon effect from the INTNO · RATIO and INTNO · NMHCPR variables would be in doubt because these variables are highly correlated with the INTNO variable, which includes no hydrocarbon dependence. The method we have chosen (Equation (14)) restricts the problem of intercorrelation to only two terms (x_1 and x_2), both of which involve hydrocarbons.* Thus, although some doubt remains as to the relative importance of these two terms, we avoid confounding of terms which involve hydrocarbons with terms which do not involve hydrocarbons.

Table 10.6 presents the results of stepwise regressions according to Equation (14). For each case (summer vs. winter and peak vs. average), the F-statistics indicated that both INTNO · RATIO and INTNO · NMHCPR are significant at a 95% confidence level. The results show a positive hydrocarbon effect that is greater for $DPKNO_2$ than for $DAVNO_2$.

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*It is interesting to note that the variables NMHCPR and RATIO are not highly intercorrelated (correlation about 0.2). However, when both variables are multiplied by INTNO, the correlation rises to about 0.9.

Table 10.6 Results of Stepwise Regressions According to Equation (14) or (15)*

Dependent Variable	Total Correlation Coefficient R	Percentage Variance Explained R^2	Constant Term $A + C_0$	$NO_2 5$ Coefficient B_1	INTNO Coefficient B'_2	INTNO. $\frac{NMHCPR}{NOX69}$ Coefficient C_1	INTNO. NMHCPR Coefficient C_2
WINTER							
$DPKNO_2$	0.78	61%	0.54	1.18	-0.05	0.029	0.00040
$DAVNO_2$	0.84	71%	0.64	0.83	0.00	0.015	0.00018
SUMMER							
$DPKNO_2$	0.79	62%	2.81	0.78	0.17	0.027	0.00043
$DAVNO_2$	0.81	65%	2.42	0.53	0.13	0.009	0.00011

*Units of all variables are in pphm. Note that all regression coefficients are significant from zero at a 95% confidence level.

Table 10.6 also shows the percentage variance explained (R^2) for the entire predictive equation. The high percentage variance explained is encouraging considering the potential errors in aerometric data and the fact that transport has been neglected in the analysis.

10.2.4 The Effect of Including Weather Variables

For daytime NO_2 in Downtown Los Angeles, data are available for seven meteorological parameters: maximum mixing height (HM), maximum daily temperature (TM), 9:00-12:00 A.M. wind speed (WS), minimum relative humidity (RH), 7:00-12:00 A.M. solar radiation (SR), pressure gradient from LAX to Palmdale (PG), and temperature gradient from LAX to Palmdale (TG). By including these variables in the empirical modeling analysis, an investigation can be made of the possibility that the observed relationships between the precursor variables and daytime NO_2 are spurious. Spurious relationships could result if a precursor variable were highly correlated with the weather parameters that govern the amount of NO_2 produced from the precursors. In such a case, the precursor variable might act as a surrogate for the weather variables.

To determine the most important meteorological parameters, logarithmic regressions were run between daytime NO_2 and the seven weather variables. Table 10.7 summarizes the results of these regressions. This table indicates that there are three key weather variables in winter (HM, TM, and WS), while there are only two key weather variables in summer (HM and TM). The signs of the dependencies are as expected, negative for HM and WS and positive for TM.

The logarithmic regressions with weather variables were also run according to a stepwise procedure. The stepwise regressions produced similar conclusions; i.e., HM, TM and WS are the three important variables in winter, while HM and TM are the two important variables in summer.

Table 10.7 Results of Logarithmic Regressions Between Daytime NO_2 and Weather Variables

	WINTER		SUMMER	
	$DPKNO_2$	$DAVNO_2$	$DPKNO_2$	$DAVNO_2$
Correlation Coefficient, R, for Logarithm of Daytime NO_2	0.72	0.73	0.65	0.55
Percentage Variance Explained in Logarithm of Daytime NO_2, R^2	52%	53%	42%	30%
Meteorological Variables	Logarithmic Regression Coefficients			
HM	-0.54**	-0.53**	-0.48**	-0.34**
TM-45	0.58**	0.46**	0.66**	0.50**
WS	-0.59**	-0.57**	0.06	-0.08
RH	0.08	0.05	-0.27*	-0.15
SR	0.20*	0.13	0.06	0.03
PG+40	0.00	0.00	0.00	0.00
TG+20	-0.02	0.05	0.00	0.00

*Significant at 99% confidence level

**Significant at 99.99% confidence level

An interesting result of the weather regression analysis is that temperature has very high significance, while solar radiation is of little significance and wind speed is important only in winter. The importance of TM can be partially explained by the hypothesis that elevated temperatures enhance the photochemical reactions that convert NO to NO_2. It is also possible that the variable TM encompasses some of the effects of WS and SR. Table 10.8 lists the linear correlation coefficients among the meteorological variables. This table shows that TM is negatively correlated with WS and positively correlated with SR. Thus, TM may partially act as a surrogate for WS and SR.

It is notable that the explanatory capability of all seven weather variables combined tends to be less than that of the two precursors, NOX69 and HC69. Table 10.7 indicates that the meteorological variables explain 30% to 52% of the variance in the logarithm of the daytime NO_2.* Logarithmic regressions of daytime NO_2 vs. the two precursor variables (as summarized in Table 10.2) explain 58% to 65% of the variance.* This conclusion was supported by other types of regressions. The nonlinear regression program, COMPLIAR, explained about 30% to 40% of the variance in daytime NO_2 in terms of the two or three key weather variables. However, COMPLIAR was able to explain about 60% to 70% of the variance in daytime NO_2 in terms of $NO_2$5, INTNO, and NMHCPR.

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*Note that for the logarithmic regressions, the percentage variance explained in $DPKNO_2$ (or $DAVNO_2$) was about 5% to 10% less than the percentage variance explained in $\ell n DPKNO_2$ (or $\ell n DAVNO_2$).

Table 10.8 Linear Correlation Coefficients Between Weather Variables and Precursor Variables

WINTER

	HM	TM	WS	RH	SR	TG	PG	NOX69	NMHCPR
HM	1.00	-0.00	0.25	-0.26	0.36	0.13	-0.02	-0.16	-0.32
TM		1.00	-0.31	-0.54	0.39	0.27	-0.68	0.36	0.40
WS			1.00	0.10	0.12	-0.15	0.29	-0.34	-0.39
RH				1.00	-0.64	-0.46	0.68	-0.32	-0.21
SR					1.00	0.28	-0.41	0.10	0.03
TG						1.00	-0.64	0.19	0.08
PG							1.00	-0.39	-0.34
NOX69								1.00	0.80
NMHCPR									1.00

SUMMER

	HM	TM	WS	RH	SR	TG	PG	NOX69	NMHCPR
HM	1.00	-0.31	0.08	-0.23	-0.03	0.67	-0.16	-0.04	-0.22
TM		1.00	-0.20	-0.45	0.38	-0.20	-0.58	0.46	0.53
WS			1.00	-0.02	0.27	0.14	0.03	-0.04	-0.08
RH				1.00	-0.50	-0.36	0.62	-0.40	-0.35
SR					1.00	0.01	-0.36	0.29	0.19
TG						1.00	-0.48	0.12	0.34
PG							1.00	-0.50	-0.46
NOX69								1.00	0.78
NMHCPR									1.00

To investigate whether inclusion of the meteorological parameters in the empirical modeling analysis would affect the observed relationships between daytime NO_2 and the precursor variables (i.e., to check whether the observed NO_2/precursor relationships might be spurious), two tests were used. The first test was based on "weather discounted" dependent variables. Weather effects were subtracted by defining new dependent variables as $DPKNO_2/DP\hat{K}NO_2$ and $DAVNO_2/DA\hat{V}NO_2$, where $DP\hat{K}NO_2$ and $DA\hat{V}NO_2$ are predicted values based on various weather regression formulas. In one case, stepwise logarithmic weather regressions were used to define $DP\hat{K}NO_2$ and $DA\hat{V}NO_2$. This analysis indicated that NO_25 and INTNO retained their significance as precursor variables, but that hydrocarbon variables (NMHCPR or NMHCPR/NOX69) lost their apparent positive effect on NO_2.* In a much more general analysis, COMPLIAR regressions were used to determine $DP\hat{K}NO_2$ and $DA\hat{V}NO_2$, and further COMPLIAR regressions were then run between the weather discounted variables and the precursors. This general analysis indicated that hydrocarbon variables, as well as NO_25 and INTNO, retained their importance.

The second test was to include the significant weather parameters as independent variables in various regressions that had previously been run with precursor variables only. It was found that these new regressions, with weather added, attributed about the same importance to NO_x variables (such as NO_25, INTNO, or NOX69) but reduced the importance assigned to hydrocarbon variables (such as NMHCPR and NMHCPR/NOX69). For instance, Table 10.9 shows the effect that including weather variables has on the hydrocarbon coefficients in the linear regression according to Equation (14). It is apparent that inclusion of weather parameters reduces the size of the hydrocarbon coefficients (especially in summer).

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*There was reason to suspect the method based on the simple logarithmic regressions. The residuals of the logarithmic weather regressions contained a strong bias. It is possible that this bias could serve to mask the hydrocarbon dependence.

All in all, the results of including weather variables in the empirical modeling analysis are inconclusive. On one hand, it can be contended that the observed effect of hydrocarbons is partly spurious. The hydrocarbon effect may be overstated because of intercorrelations between hydrocarbons and the weather factors governing NO_2 production, especially TM (see Table 10.8). On the other hand, the observed hydrocarbon effect may be real. A plausible argument can be made that including weather factors in the statistical analysis could mask the actual effect of hydrocarbons. It is encouraging that the most general method of including weather variables (using the COMPLIAR program) retained the significance of hydrocarbons.

Perhaps the best use of the analyses with weather factors is to place a caveat on our results. We will proceed with the empirical model (e.g., Equation (15) that was derived without including weather variables. However, the possibility should be kept in mind that this model may overstate the relationship between hydrocarbons and NO_2. This caveat stresses the need to conduct quantitative checks of the empirical model against smog-chamber results and against historical air quality trends.

10.3 DEPENDENCE OF NIGHTTIME NO_2 ON PRECURSORS

The second part of the empirical study for Downtown Los Angeles involves the dependence of nighttime NO_2 on precursors. The dependent variables for the nighttime period are night peak one-hour NO_2 ($NPKNO_2$) and night average

Table 10.9 Effect of Including Weather Variables in the Linear Regressions According to Equation (15)

Dependent Variable		C_1, Coefficient Of $\frac{NMHCPR}{NOX69}$	C_2, Coefficient Of NMHCPR
WINTER			
$DPKNO_2$	Without Weather	0.029	0.00040
	(With Weather)	(0.028)	(0.00034)
$DAVNO_2$	Without Weather	0.015	0.00018
	(With Weather)	(0.013)	(0.00013)
SUMMER			
$DPKNO_2$	Without Weather	0.027	0.00043
	(With Weather)	(0.015)	(0.00015)
$DAVNO_2$	Without Weather	0.009	0.00011
	(With Weather)	(0.003)	(0.00005)

NO_2 ($NAVNO_2$) as defined in Section 9.3. The two basic precursor variables are: 4:00-7:00 P.M. NO_x (NOXPM) and 2:00-4:00 P.M. (O_3AFT).

The analysis for the nighttime period turned out to be much more straightforward than the analysis for the daytime period. The main reason for this was the insigificant correlation between the nighttime precursor varibles; the correlation coefficient between NOXPM and O_3AFT was only about - 0.07. This resulted in a simplification over the daytime case which had involved high correlations between the independent variables.

Taking a hint from the daytime analysis, we decided to include initial conditions by dividing NOXPM into two parts*:

$$NO_216 = NO_2 \text{ at 3:00-4:00 PM}$$

and

$$NITENO = NOXPM - NO_216$$

To investigate the NO_2/precursor dependence, simple linear regressions were run of the form

$$\underset{(\text{or } NAVNO_2)}{NPKNO_2} = A + B_1 \cdot NO_216 + B_2 \cdot NITENO + B_3 \cdot O_3AFT \quad . \qquad (16)$$

---

*The correlations of O_3AFT to both these parts were small.

As summarized in Table 10.10, these regressions produced excellent results. The multiple correlation coefficients ranged from 0.76 to 0.90 (variance explained = 58% to 81%), and the regression coefficients for all three independent variables were highly significant. The most significant variable, as measured by the F-statistic, was $NO_2$16.

Table 10.10 Results of Nighttime Regression Analysis According to Equation (16)*

Dependent Variable	Multiple Correlation Coefficient	Percentage of Variance Explained	Regression Coefficients**			
			CONSTANT A	$NO_2$16 B_1	NITENO B_2	O_3AFT B_3
WINTER						
$NPKNO_2$	0.90	81%	-0.24	0.92	0.29	0.31
$NAVNO_2$	0.84	70%	1.23	0.58	0.12	0.16
SUMMER						
$NPKNO_2$	0.85	72%	0.70	0.88	0.51	0.09
$NAVNO_2$	0.76	58%	0.65	0.59	0.38	0.08

*Units of all pollutant variables are in pphm.

**All three independent variables were highly significant in each case. All t values were greater than 6, i.e., F-statistics were greater than 36. An F-statistic of 4 is necessary for a 95% significance level.

To obtain a better understanding of the form of the relationships, residual nighttime NO_2 was calculated according to

$$\text{Residual Nighttime } NO_2 = \text{Nighttime } NO_2 - A - B_1 \cdot NO_2 16 \qquad (17)$$

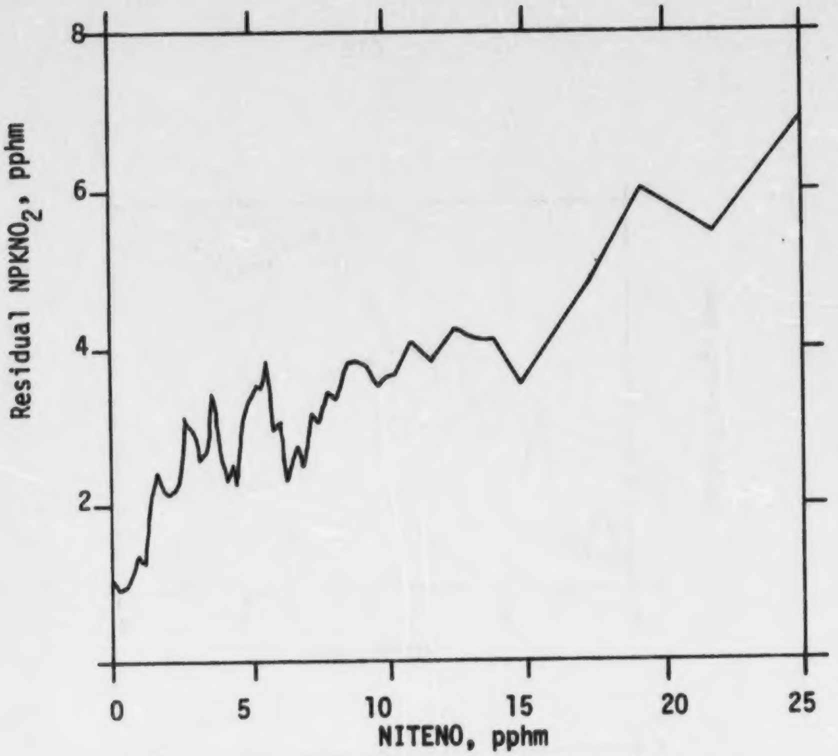
and plotted vs. NITENO. Figures 10.9 and 10.10 illustrate such plots for winter and summer, respectively. These graphs indicate that the form of the dependence on NITENO is approximately linear (note that the fluctuations in the graphs are due to statistical noise).

Figures 10.11 and 10.12 present similar plots stratified by the level of afternoon ozone. For fixed ozone level, the dependence of residual NO_2 on NITENO tends to be approximately linear. There is, however, an obvious shift from one ozone level to the next. To account for a linear dependence on NITENO that shifts with the ozone level, regressions were run of the form

$$\begin{aligned} NPKNO_2 &= A + B_1 \cdot NO_2 16 + NITENO \cdot (B_2 + B_3 \cdot O_3 \text{ AFT}) \qquad (18) \\ &= A + B_1 \cdot NO_2 16 + B_2 \cdot NITENO + B_3 \cdot NITENO \cdot O_3 \text{ AFT} . \end{aligned}$$

These regressions did yield some improvement in percentage variance explained over Equation (18); the results are summarized in Table 10.11. This particular regression form will be used in the predictive models formulated in the final section of this chapter.

There is a potential problem in the regression form represented by Equation (18). The last two terms are intercorrelated because they both contain the variable NITENO. However, the intercorrelation is not extremely



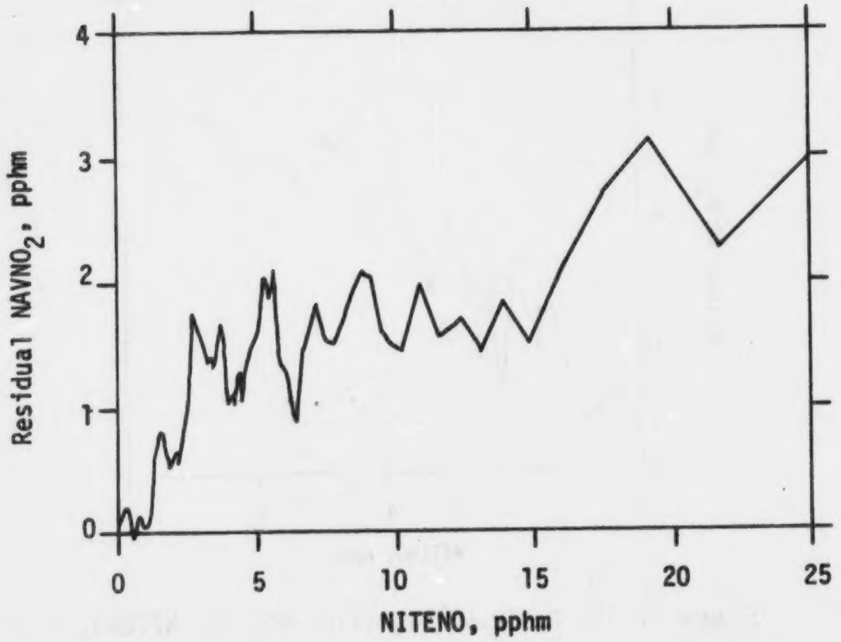


Figure 10.9 Residual Nighttime NO$_2$ vs. NITENO, Winter Season

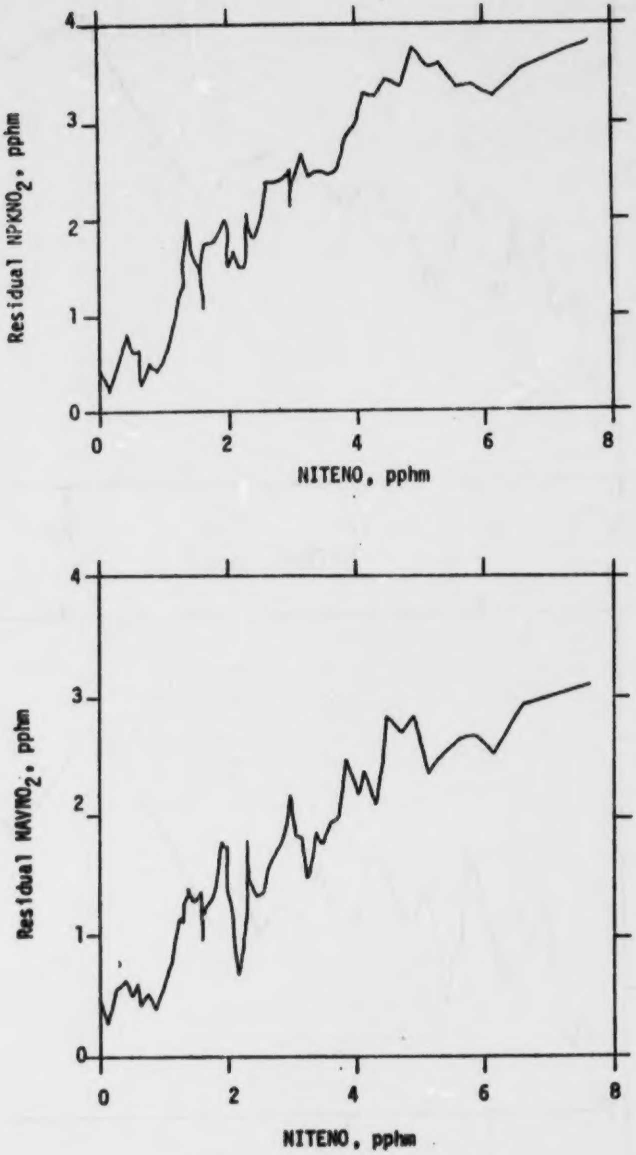


Figure 10.10 Residual Nighttime NO$_2$ vs. NITENO, Summer Season

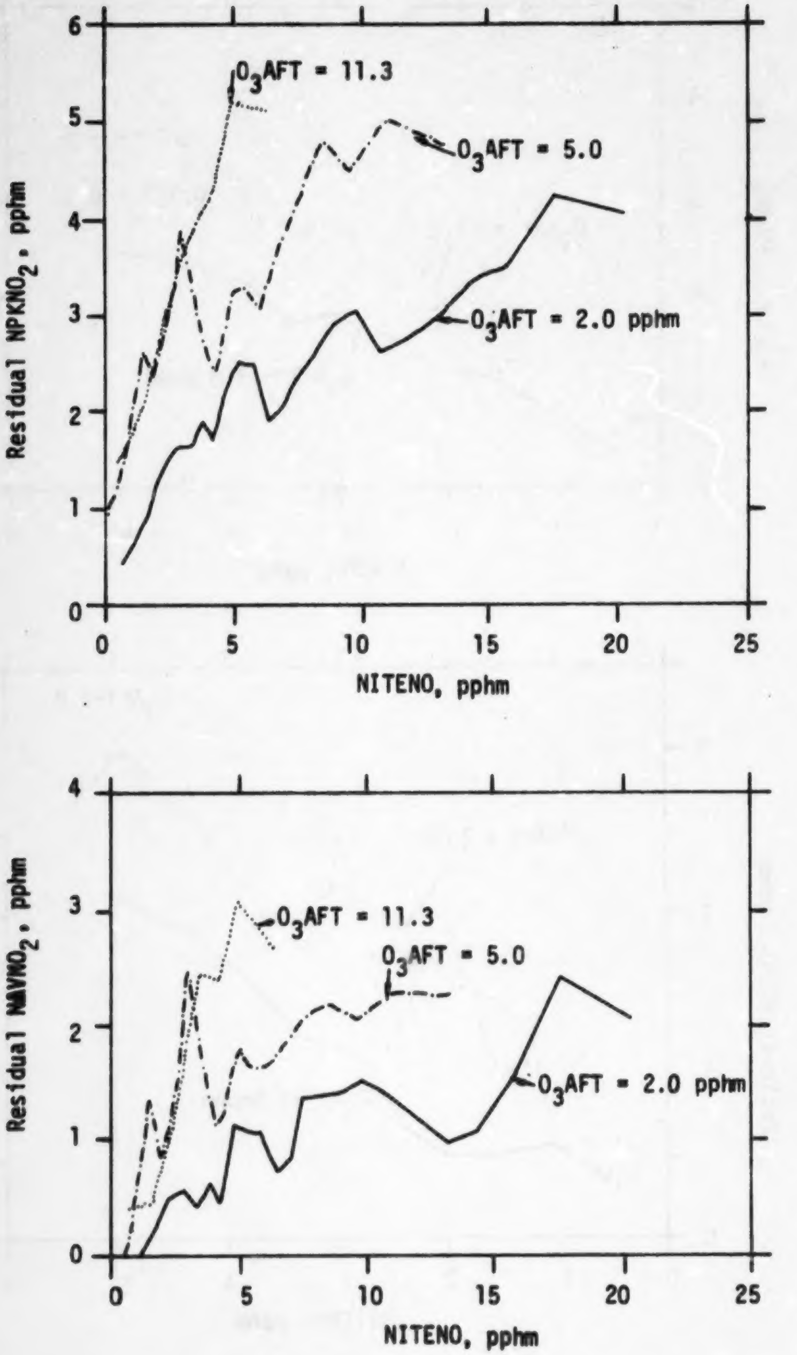
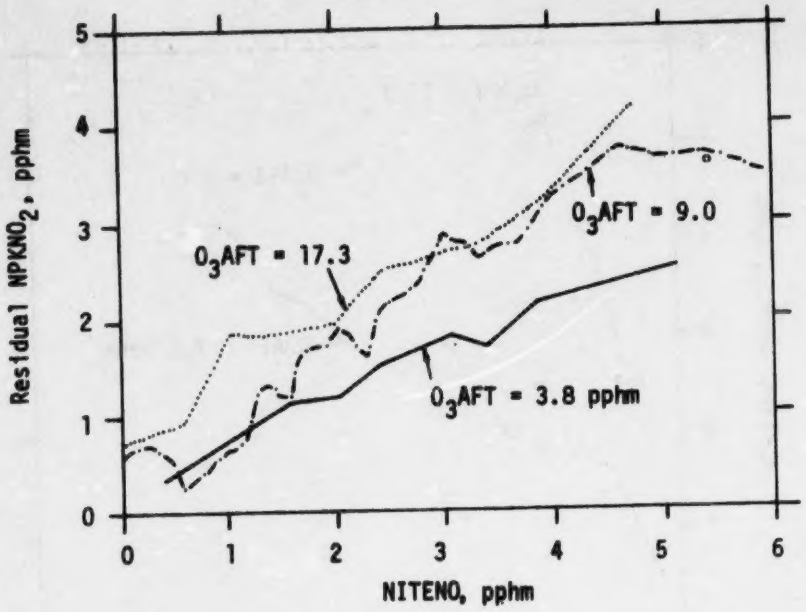


Figure 10.11 Residual Nighttime NO_2 vs. NITENO at Various Afternoon Ozone Levels, Winter Season



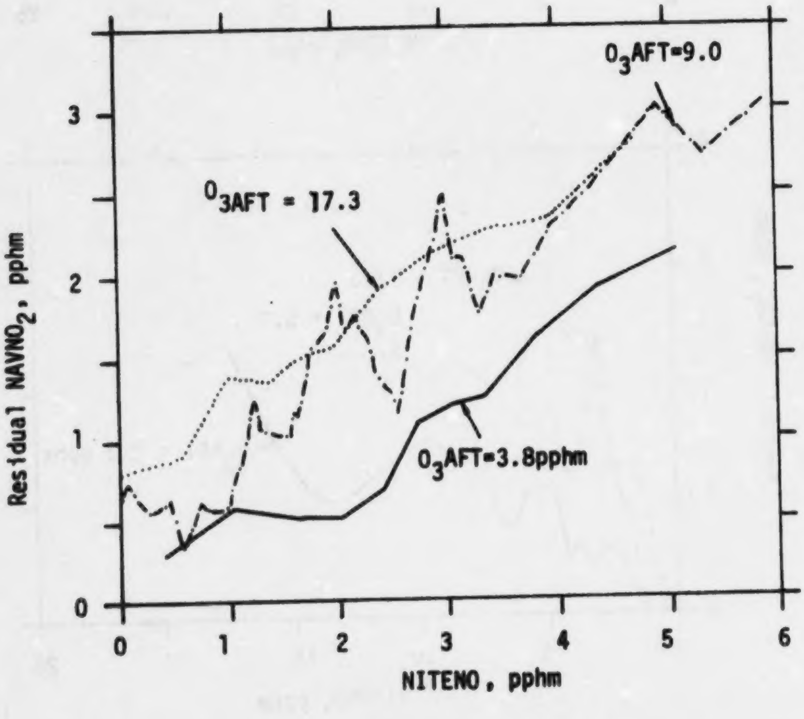


Figure 10.12 Residual Nighttime NO_2 vs. NITENO at Various Afternoon Ozone Levels, Summer Season

high (about 0.6). Also, the relative importance assigned to the oxidant term in Equation (18) turns out to be about the same as in Equation (16) (which did not involve the colinearity difficulty). Thus, the intercorrelation does not appear to affect the results in Table 10.11 significantly.

The results in Table 10.11 indicate that at least three variables are important in explaining nighttime NO_2 concentrations, the initial NO_2 ($NO_2$16), the remainder of NOXPM (NITENO), and afternoon oxidant (O_3AFT). To construct a model relating nighttime NO_2 to primary precursors (NO_x and NMHC), an assumption must be made concerning the dependence of O_3AFT on primary precursors. This assumption will be made in Section 10.4.

Table 10.11 Results of Nighttime Regression Analysis According to Equation (18)*

Dependent Variable	Multiple Correlation Coefficient	Percentage of Variance Explained	Regression Coefficients*			
			CONSTANT A	$NO_2$16 B_1	NITENO B_2	NITENO·O_3AFT B_3
WINTER						
$NPKNO_2$	0.91	82%	1.38	0.91	0.09	0.052
$NAVNO_2$	0.84	71%	2.08	0.57	0.02	0.026
SUMMER						
$NPKNO_2$	0.86	73%	1.51	0.89	0.19	0.036
$NAVNO_2$	0.77	60%	1.34	0.59	0.13	0.028

*Units of all pollutant variables are in pphm.

There is one other subtlety in the nighttime analysis, the dependence of $NO_2 16$ on the primary precursors. The simplest assumption would be that $NO_2 16$ is proportional to NO_x. However, theoretical reasoning [5] and smog-chamber evidence [4] indicate that NO_2 late in the day should bear an inverse relationship with hydrocarbons or with the hydrocarbon-to-NO_x ratio. An inverse relationship should exist because hydrocarbon reductions can suppress the photochemical reactions that consume NO_2 after it has reached a peak (see Figure 7.6). This effect might also account for our conclusion that day peak NO_2 is more sensitive to hydrocarbon reductions than is day average NO_2. To test for this effect, we ran a linear regression for each season between $NO_2 16$ and the morning hydrocarbon-to-NO_x ratio. The results were as follows:

$$\begin{aligned} &\text{Winter:} \qquad NO_2 16 = 9.7 \text{ pphm}\left[1 - 0.025\,\frac{NMHCPR}{NOX69}\right] \\ &\text{Summer:} \qquad NO_2 16 = 6.7 \text{ pphm}\left[1 - 0.018\,\frac{NMHCPR}{NOX69}\right] \end{aligned} \qquad (19)$$

The dependence of $NO_2 16$ on the hydrocarbon-to-NO_x ratio was very significant (as measured by the F-statistic) for both summer and winter.

It is possible that Equation (19) does not actually represent a causal, photochemical relationship between afternoon NO_2 and the hydrocarbon/NO_x ratio. Rather, the observed relationship may be an artifact produced by the positive correlation which exists between $NO_2 16$ and NOX69 and, in turn, the negative correlation which exists between NOX69 and NMHCPR/NOX69. We will assume that the relationship is causal and will include Equation (19) in the predictive models developed in the next section. This assumption is not very critical because the effect represented by Equation (19) is not one of the dominant aspects of the predictive models.

10.4 PREDICTIVE MODELS FOR DOWNTOWN LOS ANGELES

The previous two sections analyzed aerometric data for NO_2 and its precursors and discussed general conclusions concerning the NO_2/precursor dependence. The important precursor variables were identified, and their impact on NO_2 concentrations was illustrated using graphical techniques and regression equations. The present section develops empirical models which predict the impact that precursor control would have on NO_2 concentrations in Downtown Los Angeles. These models are based on a combination of the regression equations with certain simple physical assumptions.

The empirical models formulated here are directed toward the question: If hydrocarbon and NO_x concentrations in Downtown Los Angeles are changed by certain amounts, how would peak and average NO_2 concentrations change? Our answer to this question implicitly assumes that the general diurnal pattern of the precursor concentrations is not drastically altered when overall precursor levels are changed. Also, the empirical models do not address the question as to how precursor emission changes are related to precursor concentration changes. That is a separate problem which can be answered by diffusion models for the primary contaminants, or by rollback models if the spatial distribution of emissions is assumed constant.

It should be emphasized that the empirical models formulated below are based on NO_2/precursor relationships observed when weather variables are not included in the analysis. As noted earlier, the inclusion of weather variables indicates that the observed hydrocarbon effect might be partially spurious. Thus, it is possible that the quantitative models presented here may overstate the real effect of hydrocarbons.

Considering the limitations in our approach and the potential for spurious relationships in the regression equations, we are, in a sense, stretching our results by formulating predictive models based on the regressions. However, the reason for extending the results is not to derive a quantitative tool that is ready for application without qualifications to control strategy analysis. Rather, the reason is to put our conclusions in a form that can be checked quantitatively by comparison with historical air quality trends and with predictions of smog-chamber models, and to provide control guidelines that are consistent with observations of aerometric data.

10.4.1 Predictive Model for Annual Mean NO_2

The model for annual mean NO_2 must be constructed from submodels for the two seasons and the two times of day. Because of the importance of initial conditions, these submodels must include linkage between the daytime and nighttime periods. The following discussion will first deal with each of the four submodels individually. These submodels will then be synthesized into a single predictive model for annual mean NO_2.

Daytime Average NO_2, Winter Season

Section 10.2.3 developed regression formulas which indicated the dependence of daytime average NO_2 on precursors. The winter regression formula (summarized in Equation (15) and Table 10.6) included four terms,

$$\begin{aligned} DAVNO_2 &= 0.64 + 0.83NO_25 + INTNO\left[0.015\frac{NMHCPR}{NOX69} + 0.00018\ NMHCPR\right] \\ &= 0.64 + 0.83NO_25 + 0.015\ INTNO\cdot\frac{NMHCPR}{NOX69} + 0.00018\ INTNO\cdot NMHCPR, \qquad (20) \end{aligned}$$

with all pollutant variables in units of pphm.

Substituting in average pollutant values for the winter season (NO_25 = 6.6 pphm, NOX69 = 30.1 pphm, INTNO = 23.5 pphm, and NMHCPR = 149 pphm), this equation yields

$$\mathrm{DAVNO_2} = \overset{\mathrm{I}}{0.64} + \overset{\mathrm{II}}{5.48} + \overset{\mathrm{III}}{1.74} + \overset{\mathrm{IV}}{0.63} \qquad (21)$$

$$= 8.49 \text{ pphm}$$

for the mean value of daytime average NO_2 in the winter season. As expected, this is close to the actual winter daytime mean of 8.54 pphm.

A predictive model for daytime average NO_2 can be formulated by making assumptions as to how each of the four terms in Equation (21) will change when the precursors, NO_x and hydrocarbons, are controlled. We will make the following assumptions:

Term I: This is the remainder term that we did not explain in terms of NOX69 and NMHCPR. It is presumably due to factors(such as post-9:00 A.M. emissions) that were not accounted for in our analysis. Fortunately, this is not a large term, and our assumption will not be critical. We will make the simple assumption that it is directly proportional to NO_x control and independent of hydrocarbon control.

Term II: This is the initial NO_2 term. It will depend on the effect that precursor control has on overnight NO_2. Thus, it requires a coupling with the nighttime models. As will be shown later (Table 10.14), nighttime average NO_2 is proportional to NO_x control and essentially independent of hydrocarbon control Thus, we conclude that initial NO_2 should be proportional to NO_x control and independent of hydrocarbon control.

Term III: As indicated by Equation (20), this term involves the precursors in the form INTNO·NMHCPR/NOX69. The effect of NO_x control on this term should be zero, a cancelling of proportionality between INTNO in the numerator and NOX69 in the denominator. Thus, this term should be directly proportional to hydrocarbon control.

Term IV: As indicated by Equation (20), this term involves INTNO·NMHCPR. Thus, it should be proportional to the product of NO_x and hydrocarbons.

With these assumptions, we can calculate the effect that given amounts of precursor control will have on daytime average NO_2 in the winter season. For instance, assume we control NO_x by 20% and hydrocarbons by 50%, then the four terms would change as follows:

I:	0.64 x 80%	0.51
II:	5.48 x 80%	4.38
III:	1.74 x 50%	0.87
IV:	0.63 x 80% x 50%	0.25
	New Daytime Average =	6.01
	Percentage Change =	$\frac{6.01 - 8.49}{8.49} = -29\%$

Using this method, we can calculate the impact that various degrees of precursor control have on daytime average NO_2 in the winter season. Table 10.12 presents the results in terms of percentage changes in winter daytime average NO_2. The model should not be used for very large degrees of control ($\sim$ 80% or more) since we would be extrapolating beyond the degree of variation which we observed in the morning precursor levels. To predict winter daytime average NO_2 at various degrees of control, the percentage reductions in Table 10.12 should be applied to the actual value for daytime average NO_2 (8.54 pphm) rather than the computed value (8.49 pphm).

Table 10.12 Percentage Changes in Winter Daytime Average NO_2 at Downtown Los Angeles as a Function of NO_x and Hydrocarbon Control

NMHC CONTROL ↓ (Percentage Changes from 1969-1974 Level)	NO_x CONTROL → (Percentage Changes from 1969-1974 Level)				
	+20%	0%	-20%	-40%	-60%
+20%	+22%	+6%	-11%	-27%	-43%
0%	+16%	0%	-16%	-32%	-48%
-20%	+10%	-6%	-21%	-37%	-52%
-40%	+4%	-11%	-26%	-42%	-57%
-60%	-2%	-17%	-32%	-47%	-62%

Table 10.12 indicates that hydrocarbon and NO_x control would both reduce daytime average NO_2. For a given level of hydrocarbon control, NO_x reductions have a slightly less than proportional impact on winter daytime average NO_2. For instance, with no hydrocarbon control, an NO_x reduction of 60% produces a decrease of only 48% in winter daytime average NO_2. The relationship is not exactly proportional, since reducing NO_x has the side effect of increasing the hydrocarbon-to-NO_x ratio. The effect of hydrocarbon control is considerably less than the effect of NO_x control. Sixty-percent hydrocarbon control with no NO_x control reduces winter daytime average NO_2 by 17%.

Daytime Average NO_2, Summer Season

The regression equation for daytime average NO_2 in the summer season (summarized in Equation (15) and Table 10.6) was of the form

$$DAVNO_2 = 2.42 + 0.53\,NO_25 + 0.13\,INTNO + 0.009\,INTNO \cdot \frac{NMHCPR}{NOX69} + 0.00011\,INTNO \cdot NMHCPR \tag{22}$$

with units of all pollutant variables in pphm. Substituting in average pollutant values for the summer season (NO_25 = 5.3 pphm, NOX69 = 18.9 pphm, INTNO = 13.6 pphm, and NMHCPR = 120 pphm) in Equation (22) yields

$$\begin{aligned} DAVNO_2 &= \overset{I}{2.42} + \overset{II}{2.81} + \overset{III}{1.77} + \overset{IV}{0.78} + \overset{V}{0.18} \\ &= 7.96 \text{ pphm} \quad . \end{aligned} \tag{23}$$

This is close to the actual summer daytime mean NO_2, 7.94 pphm.

To form a predictive model, we make the following assumptions for each term:

Term I: This term is assumed proportional to NO_x and independent of hydrocarbons (see earlier discussion).

Term II: As indicated by coupling with the nighttime model, this term should be proportional to NO_x and independent of hydrocarbons (see earlier discussion).

Term III: This term involves the variable INTNO in Equation (22). It should also be proportional to NO_x and independent of hydrocarbons.

Term IV: This term should be proportional to hydrocarbons and independent of NO_x (see earlier discussion).

Term V: This term should be proportional to the product of NO_x and hydrocarbons (see earlier discussion).

Following the procedures outlined for average NO_2 in winter, the impact of NO_x and hydrocarbon control on summer daytime average NO_2 was calculated. Table 10.13 presents the results. Again, the effect of NO_x is more important than the effect of hydrocarbons. A 60% NO_x reduction (with no hydrocarbon control) decreases summer daytime average NO_2 by 54%, while a 60% hydrocarbon reduction (with no NO_x control) decreases NO_2 by only 7%. Compared with Table 10.12, Table 10.13 indicates that NO_x control is slightly more important in summer than in winter, and that hydrocarbon control is less important in summer than in winter.

Table 10.13 Percentage Changes in Summer Daytime Average NO_2 at Downtown Los Angeles as a Function of NO_x and Hydrocarbon Control*

NMHC CONTROL ↓ (Percentage Changes from 1969-1974 Level)	NO_x CONTROL → (Percentage Changes from 1969-1974 Level)				
	+20%	0%	-20%	-40%	-60%
+20%	+21%	+2%	-16%	-34%	-52%
0%	+18%	0%	-18%	-36%	-54%
-20%	+16%	-2%	-20%	-38%	-56%
-40%	+13%	-5%	-23%	-41%	-58%
-60%	+11%	-7%	-25%	-43%	-61%

*To calculate summer daytime average NO_2 levels, these percentage changes should be applied to 7.94 pphm.

Nighttime Average NO_2, Winter Season

Section 10.3 develops regression equations which indicate the dependence of nighttime average NO_2 on precursors. The winter regression equation (summarized by Equation (18) and Table 10.11) included four terms,

$$NAVNO_2 = 2.08 + 0.57\ NO_216 + 0.02\ NITENO + 0.026\ NITENO \cdot O_3AFT \quad (24)$$

with all pollutant variables in units of pphm.

If we substitute in average values for the pollutant variables in winter (NO_216 = 8.3 pphm, NITENO = 7.0 pphm, and O_3AFT = 4.9 pphm), this equation yields

$$\begin{array}{lccccccc} & & \text{I} & & \text{II} & & \text{III} & & \text{IV} \\ NAVNO_2 & = & 2.08 & + & 4.71 & + & 0.14 & + & 0.89 \\ & = & 7.82\ \text{pphm.} \end{array}$$

This calculated value is close to the actual nighttime NO_2 average in winter, 7.66 pphm.

A predictive model for nighttime average NO_2 can be formulated by making the following assumptions concerning the dependence of each term on the primary precursors:

Term I: This is the remainder term that we did not relate directly to the precursors. The assumption for this term is somewhat arbitrary. We will make the simple assumption that it is directly proportional to NO_x control and independent of hydrocarbon control.

Term II: This is the initial NO_2 term for the nighttime period. As indicated by Equation (19), initial NO_2 for the nighttime period bears a slight inverse relation with the hydrocarbon-to-NO_x ratio.

Using existing hydrocarbon-to-NO_x ratios as a starting point, this effect can be approximately accounted for by taking this term to be $5.35\ NO_x \left[1 - 0.12 \frac{HC}{NO_x}\right]$, where NO_x and HC represent the control variables. This formula should only be valid for moderate levels of control, i.e., NO_x between -60% to +60% and HC between -60% to +60%.

Term III: This term involves the precursor, NITENO. It should be directly proportional to NO_x and independent of hydrocarbons.

Term IV: As indicated by Equation (24), this term involves NITENO·O_3AFT. An assumption is required as to the dependence of O_3AFT on the control variables. This assumption will not be critical since Term IV is relatively small. We will make the assumption that O_3AFT in Downtown Los Angeles is proportional to the hydrocarbon/NO_x ratio. Thus, Term IV would be directly proportional to hydrocarbons and independent of NO_x (the NO_x effect is cancelled by multiplying NITENO times the hydrocarbon/NO_x ratio).

Following procedures outlined previously, the above assumptions can be used to calculate the effect of precursor control on winter nighttime average NO_2. Table 10.14 presents the results. Table 10.14 indicates that changes in nighttime average NO_2 are almost directly proportional to NO_x control. Hydrocarbon control is slightly beneficial, but the effect is essentially negligible. It appears that the NO_2 decreases that hydrocarbon control brings in Term IV (through oxidant reductions) are neutralized by the NO_2

increases that hydrocarbon control brings in Term II (through increased afternoon NO_2 levels).

Table 10.14 Percentage Changes in Summer Nighttime Average NO_2 at Downtown Los Angeles as a Function of NO_x and Hydrocarbon Control*

NMHC CONTROL ↓ (Percentage Changes from 1969-1974 Level)	NO_x CONTROL → (Percentage Changes from 1969-1974 Level)				
	+20%	0%	-20%	-40%	-60%
+20%	+20%	+1%	-19%	-38%	-57%
0%	+19%	0%	-19%	-39%	-58%
-20%	+19%	-1%	-20%	-39%	-59%
-40%	+18%	-1%	-21%	-40%	-59%
-60%	+17%	-2%	-21%	-41%	-60%

*To calculate winter nighttime average NO_2 levels, these percentage changes should be applied to 7.66 pphm.

Nighttime Average NO_2, Summer Season

Following procedures similar to those discussed above, Equation (18) and Table 10.11 can be used to calculate the effect of NO_x and hydrocarbon control on summer nighttime average NO_2. Table 10.15 presents these results.

As was the case with winter nighttime average NO_2, the summer nighttime average is almost directly proportional to NO_x control. Hydrocarbon control yields almost negligible benefits.

Table 10.15 Percentage Changes in Summer Nighttime Average NO_2 at Downtown Los Angeles as a Function of NO_x and Hydrocarbon Control*

NO_x CONTROL →
(Percentage Changes from 1969-1974 Level)

↓ NMHC CONTROL
(Percentage Changes from 1969-1974 Level)

	+20%	0%	-20%	-40%	-60%
+20%	+20%	+1%	-18%	-37%	-57%
0%	+19%	0%	-19%	-38%	-57%
-20%	+18%	-1%	-20%	-39%	-58%
-40%	+17%	-2%	-21%	-40%	-59%
-60%	+17%	-3%	-22%	-41%	-60%

*To calculate summer nighttime average NO_2 levels, these percentage changes should be applied to 5.73 pphm.

Annual Average NO_2

To arrive at an empirical model for annual average NO_2, we must combine the results for daytime and nighttime and for the two seasons. For each level of precursor control, the predicted NO_2 level for each season and time of day is calculated by applying the percentage reductions listed in Tables 10.12 through 10.15 to the existing NO_2 average (1969-1974) for that season and time of day. The annual average is then computed according to the tautology

$$\text{Annual Average} \equiv \frac{1}{2}\left[\frac{10}{24}\text{DWA} + \frac{14}{24}\text{NWA}\right] + \frac{1}{2}\left[\frac{10}{24}\text{DSA} + \frac{14}{24}\text{NSA}\right] , \qquad (25)$$

where

DWA = daytime winter average NO_2
NWA = nighttime winter average NO_2
DSA = daytime summer average NO_2
NSA = nighttime summer average NO_2

The weights of one-half are used for the two seasons, because each season represents six months. The 10/24 and 14/24 weights are used for daytime and nighttime, respectively, because the daytime average represents 10 hours while the nighttime average represents 14 hours.

The results for annual average NO_2 at Downtown Los Angeles are summarized in Table 10.16. Table 10.16a lists percentage changes in annual average NO_2, while Table 10.16b lists predicted annual average NO_2 levels. These results indicate that changes in annual average NO_2 will be almost directly proportional to NO_x changes, with a slight beneficial impact due to hydrocarbon reductions. The relationship to NO_x is not exactly proportional because NO_x reductions would have the side effect of increasing the HC/NO_x ratio. To attain the federal air quality standard for annual average NO_2 would require approximately a 31% reduction in NO_x levels if hydrocarbons remained constant. If hydrocarbons were reduced by 60%, only a 23% reduction in NO_x levels would be required for attainment.

As indicated by Tables 10.12 through 10.15, the beneficial impact of hydrocarbon control would be accrued almost entirely during the daytime period. A 60% reduction in hydrocarbons (with no NO_x control) would result in a 12% decrease in daytime average NO_2 but only a 2% decrease in nighttime average NO_2. The impact of hydrocarbon control would also be significantly greater for daytime average NO_2 in winter than for daytime average NO_2 in summer.

Table 10.16 The Effect of NO_x and Hydrocarbon Control on Annual Average NO_2 at Downtown Los Angeles

Table 10.16a Percentage Changes in Annual Average NO_2

	NO_x CONTROL → (Percentage Changes from 1969-1974 Level)				
NMHC CONTROL ↓ (Percentage Changes from 1969-1974 Level)	+20%	0%	-20%	-40%	-60%
+20%	+21%	+ 2%	-16%	-34%	-53%
0%	+18%	0%	-18%	-36%	-55%
-20%	+16%	- 2%	-20%	-38%	-57%
-40%	+13%	- 5%	-23%	-41%	-59%
-60%	+11%	- 7%	-25%	-43%	-61%

Table 10.16b Annual Average NO_2 Levels, pphm

NO_x CONTROL →
(Percentage Changes from 1969-1974 Level)

NMHC CONTROL ↓ (Percentage Changes from 1969-1974 Level)	+20%	0%	-20%	-40%	-60%
+20%	8.9	7.5	6.2	4.8*	3.5*
0%	8.7	7.3	6.0	4.7*	3.3*
-20%	8.5	7.2	5.8	4.5*	3.2*
-40%	8.3	7.0	5.7	4.4*	3.0*
-60%	8.2	6.8	5.5	4.2*	2.9*

*Attains federal standard of 5.3 pphm (100 $\mu g/m^3$)

10.4.2 Predictive Model for Yearly One-Hour Maximum NO_2

In examining yearly one-hour maximum NO_2, it appears sufficient to restrict the analysis to the daytime period. Table 10.17 lists the days in our processed data base with the five highest one-hour NO_2 concentrations for winter and summer, and for daytime and nighttime. It is evident that the most extreme one-hour levels of NO_2 tend to occur during the daytime period.

Table 10.17 Days in the Processed Data Base with Extreme One-Hour NO_2 Levels in Downtown Los Angeles (1969 to 1974)

DAYTIME		NIGHTTIME	
Winter	Summer	Winter	Summer
74 pphm (3/29/71)	66 pphm (5/15/70)	46 pphm (1/17/71)	31 pphm (5/14/70)
58 pphm (10/16/73)	57 pphm (5/16/70)	45 pphm (1/19/71)	21 pphm (9/28/73)
56 pphm (11/9/71)	53 pphm (5/14/70)	43 pphm (1/18/71)	20 pphm (4/1/70)
55 pphm (11/24/71)	50 pphm (7/4/70)	41 pphm (1/31/71)	20 pphm (7/8/70)
52 pphm (10/17/73)	45 pphm (9/8/71)	40 pphm (2/11/71)	20 pphm (5/15/70)

It also appears that that summer daytime maxima are slightly smaller than the winter daytime maxima. An examination of all the data for Downtown Los Angeles (a larger data set than our processed data base), indicates that the typical winter maximum for the 1969-1974 period is around 60 pphm, while the typical summer maximum is around 50 pphm. Since the summer maximum is not small compared with the winter maximum, our analysis for yearly maximum one-hour NO_2 should consider both the summer and winter daytime periods.

In formulating predictive models for yearly maximum one-hour NO_2 concentrations, procedures were followed analogous to those used for annual mean concentrations. Since the analysis for the yearly maximum is restricted to the daytime period, the appropriate regression formulas are given by Equation (15) and Table 10.6. One new problem arose in the analysis of yearly maxima. The regression formulas for daytime peak NO_2 are actually applicable only to average conditions; the formulas are based on all days in the data base. Insufficient data were available to develop separate regression formulas for the few days with extreme NO_2 concentrations. The most realistic use of the regression formulas would be to predict seasonal averages of daily maxima, not yearly one-hour maxima. When applied to days of extreme NO_2 levels, the regression equations tended to under predict the one-hour maxima by as much as 40%. To circumvent this problem, the predictive model was formulated with the regression formulas by entering the precursor levels ($NO_2$5, INTNO, and NMHCPR) associated with the most extreme days of NO_2 concentrations. The percentage change indicated by this model was then applied to the actual one-hour maximum (60 pphm in winter and 50 pphm in summer).

The results of the predictive models for yearly maximal NO_2 concentrations in summer and winter are presented in Tables 10.18 and 10.19. These tables show that the effect of hydrocarbon control on maximal NO_2 levels in Downtown Los Angeles is almost as great as the effect of NO_x control. Hydrocarbon control has a slightly greater impact in winter than in summer. Applying the percentage changes in Tables 10.18 and 10.19 to the typical winter and summer maxima (60 pphm and 50 pphm, respectively) indicates that the yearly maximum would tend to occur in winter for all degrees of control listed in the tables. Thus, Table 10.18 (the winter case) can be considered as representative of the one-hour maximum for the entire year.*

Table 10.20 lists predicted values for yearly one-hour NO_2 maxima as a function of NO_x and hydrocarbon control This table has been derived by applying the percentage changes in Table 10.18 to the typical winter maximum

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*In years with unusual meteorology, the yearly maximum may actually occur in summer. Rather than complicate the predictive model, we will neglect this possibility and deal with the winter maximum only.

Table 10.18 Percentage Changes in Winter Yearly Peak One-Hour NO_2 as a Function of NO_x and Hydrocarbon Control

NO_x CONTROL →

(Percentage Changes from 1969-1974 Level)

NMHC CONTROL ↓ (Percentage Changes from 1969-1974 Level)	+20%	0%	-20%	-40%	-60%
+20%	+26%	+10%	- 6%	-21%	-37%
0%	+15%	0%	-15%	-30%	-44%
-20%	+ 4%	-10%	-24%	-38%	-52%
-40%	- 8%	-20%	-33%	-46%	-59%
-60%	-19%	-31%	-42%	-54%	-66%

Table 10.19 Percentage Changes in Summer Yearly Peak One-Hour NO_2 as a Function of NO_x and Hydrocarbon Control.

NO_x CONTROL →

(Percentage Changes from 1969-1974 Level)

NMHC CONTROL ↓ (Percentage Changes from 1969-1974 Level)	+20%	0%	-20%	-40%	-60%
+20%	+24%	+ 8%	- 9%	-25%	-42%
0%	+16%	0%	-16%	-32%	-47%
-20%	7%	- 8%	-23%	-38%	-53%
-40%	- 1%	-15%	-30%	-44%	-59%
-60%	- 9%	-23%	-37%	-50%	-64%

Table 10.20 Yearly One-Hour Maximum NO_2 Levels in Downtown Los Angeles as a Function of Hydrocarbon and NO_x Control (All Values pphm)

NO_x CONTROL ⟶
(Percentage Changes from 1969-1974 Level)

⟵ NMHC CONTROL (Percentage Changes from 1969-1974 Level)	+20%	0%	-20%	-40%	-60%
+20%	76	66	57	47	38
0%	69	60	51	42	33
-20%	62	54	46	37	29
-40%	55	48	40	32	25*
-60%	49	42	35	27	20*

*Attains the California one-hour NO_2 standard of 25 pphm

(60 pphm) for the 1969-1974 period. Table 10.20 indicates that hydrocarbon control would be nearly as important as NO_x control for attaining the one-hour California NO_2 standard in Downtown Los Angeles.

The significance of hydrocarbon control for yearly maximum one-hour NO_2 in Downtown Los Angeles is somewhat surprising. However, it is actually not implausible from a physical viewpoint. Reducing the hydrocarbon-to-NO_x ratio should delay the formation of maximal NO_2. This delay is particularly important in Downtown Los Angeles because dispersive conditions become much stronger late in the morning as the sea breeze establishes and the mixing height elevates.

Because of the uncertainties in our analysis, it will be important to check the empirical models quantitatively against smog-chamber results and against historical air quality trends. These checks will be conducted in Chapter 12 of this report. Qualitatively, the air quality trends discussed in Part I of this study provide reason for encouragement. Part I demonstrates that maximal NO_2 levels in central/coastal Los Angeles decreased slightly in the past decade even though NO_x emissions and ambient NO_x levels increased significantly. This could be the result of the hydrocarbon control that has been achieved in the central/coastal parts of Los Angeles.

One further remark should be made in regard to the predictive models summarized by Tables 10.12 through 10.20. These tables list the changes in ambient NO_2 that should result from NO_x and hydrocarbon control, but they do not quantify the errors in the predictions. Based on the statistical errors in the regression coefficients which underly the models, it would be possible to compute error bounds. However, these statistical error bounds would have little meaning because they would not be representative of the conceptual limitations inherent in the models. As noted in Section 7.2.4, these limitations include the neglect of transport, the omission of meteorology, and the assumption that precursor changes produced mostly by meteorology can be used to model the effect of control strategies. It is not possible to quantify the potential errors that arise because of these fundamental limitations in the models.

10.5 REFERENCES

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11.0 EMPIRICAL MODELS APPLIED TO VARIOUS CITIES

Chapter 10 of this report formulates statistical models of the NO_2/precursor relationship at Downtown Los Angeles. The investigation results in an empirical control model based on a series of linear regression equations and on certain simple physical assumptions. This chapter uses the same procedure to derive empirical control models for 7 other locations: Lennox (CA), Azusa (CA), Pomona (CA), Denver, Chicago, Houston/Mae, and Houston/Aldine.

11.1 GENERAL METHODOLOGY

The empirical NO_2 control model for Downtown Los Angeles was based on regression equations for daytime NO_2 (Equations (12), (14), and (15)), regression equations for nighttime NO_2 (Equations (18) and (19)), and simple physical assumptions which transformed these equations into predictive control models (Section 10.4). The exact procedure is used here to derive empirical control models for 7 other cities. This section provides a brief summary of that procedure. The reader is referred to Chapters 9 and 10 for more detailed descriptions of the procedures and for exact definitions of the variables used.

The empirical control models for all 10 cities are based on regression equations which do not explicitly include weather variables. As noted in Chapter 10, the inclusion of weather variables raises questions as to whether the observed dependence of NO_2 hydrocarbons is real or whether it is partially an artifact produced by unaccounted for weather variables. This stresses the need to check the results of the empirical models against historical air quality trends and smog-chamber experiments. These checks will be performed in subsequent chapters.

11.1.1 Regression Equations for Daytime NO_2

The dependent variables for the daytime analysis are daytime peak one-hour NO_2 ($DPKNO_2$) and daytime average NO_2 ($DAVNO_2$). Regressions are run (separately for $DPKNO_2$ and $DAVNO_2$, separately for winter and summer) of the form:

$$\underset{(\text{or } DAVNO_2)}{DPKNO_2} = A + B_1 \cdot NO_2 5 + B_2 \cdot INTNO \quad . \tag{26}$$

The B_1 term represents the contribution of early-morning NO_2 carried over from the previous night. The B_2 term represents the contribution from the conversion of NO (both carry-over NO and early-morning NO emissions). The constant (usually small) represents the contribution from other factors, such as late-morning NO emissions.

It is assumed that hydrocarbons (NMHCPR) affect daytime NO_2 by governing the amount of INTNO converted to NO_2. The effect of hydrocarbons is estimated by performing a stepwise regression,

$$y = C_0 + C_1X_1 + C_2X_2 \ , \tag{27}$$

where

$$y = \underset{(\text{or } DAVNO_2)}{DPKNO_2} - A - B_1 \cdot NO_2 5 - B_2 \cdot INTNO,$$

$$X_1 = [RATIO - \overline{RATIO}] \cdot INTNO,$$

$$X_2 = [NMHCPR - \overline{NMHCPR}] \cdot INTNO,$$

$$RATIO = NMHCPR/NOX69,$$

and "$\overline{\quad\quad}$" = average values.

This results in a final equation of the form

$$\begin{array}{l} DPKNO_2 = (A + C_0) + B_1 \cdot NO_2 5 + INTNO \cdot [B_2' + C_1 \cdot RATIO + C_2 \cdot NMHCPR] \ , \\ \text{(or } DAVNO_2 \text{)} \end{array} \tag{28}$$

$$\text{where } B_2' = B_2 - C_1 \cdot \overline{RATIO} - C_2 \cdot \overline{NMHCPR}.$$

11.1.2 Regression Equations for Nighttime NO_2

The basic equations for nighttime NO_2 are obtained by stepwise regressions (separately for $NPKNO_2$ and $NAVNO_2$, separately for winter and summer) of the form

$$\begin{array}{l} NPKNO_2 = A + B_1 \cdot NO_2 16 + B_2 \cdot NITENO + B_3 \cdot NITENO \cdot O_3 AFT \ . \\ \text{(or } NAVNO_2 \text{)} \end{array} \tag{29}$$

The second term indicates the contribution of NO_2 carried over from the afternoon. The third and fourth terms represent the contribution of NO (carried over from the afternoon or emitted during the early evening). The conversion of NO to NO_2 is allowed to depend on the afternoon oxidant level (fourth term). The constant, A, represents contributions from other factors, such as nighttime NO emissions.

Since the afternoon NO_2 level ($NO_2 16$) may depend on early-morning hydrocarbons, a regression (separately for winter and summer) is also run of the form

$$NO_2 16 = D_0 + D_1 \cdot RATIO, \tag{30}$$

where RATIO is the morning NMHCPR/NOX69 level.

11.1.3 Empirical Control Models

The regression equations are transformed into empirical control models by adding certain physical assumptions. For the daytime models, based on

Equation (28), the assumptions are listed in Table 11.1.

Table 11.1 Assumptions to Convert Equation (28) into a Control Model for Daytime NO_2

Term in Equation (28)	Control Assumption	Remarks
$A + C_0$	Proportional to NO_x Independent of HC	This is the simplest assumption to make. Fortunately, this assumption is usually not critical.
$B_1 \cdot NO_25$	Proportional to NO_x Independent of HC	This assumption is supported by the models for nighttime average NO_2.
$B_2' \cdot INTNO$	Proportional to NO_x Independent of HC	
$C_1 \cdot RATIO \cdot INTNO$	Independent of NO_x Proportional to HC	The effect of NO_x control is cancelled by proportionality between INTNO and NOX69 (denominator of RATIO).
$C_2 \cdot NMHCPR \cdot INTNO$	Proportional to the product of NO_x and HC	

The nighttime model is formed by inserting Equation (30) into Equation (29). The assumptions which transform the equation into a control model are listed in Table 11.2.

Table 11.2 Assumptions to Convert Equation (29) into a Control Model for Nighttime NO_2

Term in Equation (29)	Control Assumption	Remarks
A	Proportional to NO_x Independent of HC	This is the simplest assumption to make; it is usually not critical
$B_1 \cdot D_0$	Proportional to NO_x Independent of HC	This term is obtained by substituting Equation (30) into Equation (29). The parameter D_0 should be directly proportional to NO_x.
$B_1 \cdot D_1 \cdot RATIO$	Independent of NO_x Proportional to HC	This term is obtained by substituting Equation (30) into Equation (29). The parameter D_1 should be directly proportional to NO_x.
$B_2 \cdot NITENO$	Proportional to NO_x Independent of HC	
$B_3 \cdot NITENO \cdot O_3AFT$	Independent of NO_x Proportional to HC	It is implicitly assumed that O_3AFT is porportional to the HC/NO_x ratio. This assumption should be approximately true for many central-city locations. However, it may not hold for Houston or for downwind sites in Los Angeles (e.g., Azusa or Pomona). Fortunately, this assumption is usually not critical.

11.2 CONTROL MODELS FOR VARIOUS CITIES

Using the procedures outlined in the previous section and in Chapter 10, this section formulates empirical control models for 7 cities. For each location, a model is developed for annual mean NO_2 and yearly peak one-hour NO_2. The model for annual mean NO_2 involves synthesis of four submodels, for daytime average NO_2 and nighttime average NO_2 in both winter and summer.

The synthesis is based on Equation (25), page 234. The model for yearly peak one-hour NO_2 is developed by using the regression equation for $DPKNO_2$ corresponding to the season and time of day when the yearly peak occurs. "Worst-case" conditions are used in the regression equation for $DPKNO_2$.

The following discussions deal only with the resultant control models for each city. The regression equations which serve as the foundation of the control models are presented in Appendix D.

11.2.1 Lennox, California

The Lennox monitoring site is located about eleven miles southeast of Downtown Los Angeles and three miles from the coastline. Like Downtown Los Angeles, Lennox is within the area of high emission density that spreads over the central/coastal parts of the Los Angeles basin. However, Lennox is in the upwind part of the source-intensive area, while Downtown Los Angeles is in the center of the area.

The empirical control model for annual mean NO_2 at Lennox is summarized in Table 11.3. Percentage changes in annual average NO_2 at Lennox are listed for various changes in NO_x and NMHC concentrations at Lennox. Also presented are predicted annual average NO_2 concentrations (Table 11.3b). As was the case for Downtown Los Angeles (Section 10.4.1), annual mean NO_2 at Lennox is essentially directly proportional to NO_x, with minute benefits accrued from NMHC control. Attainment of the federal annual mean standard for NO_2 must be accomplished through NO_x control.

The submodels for annual mean NO_2 at Lennox indicate that nearly all the benefit from NMHC control occurs in the daytime NO_2 average rather than the nighttime NO_2 average. Also, the effect of hydrocarbons is greater for winter daytime NO_2 than summer daytime NO_2. These patterns are totally consistent with the corresponding submodels for Downtown Los Angeles.

Table 11.3 The Effect of NO$_x$ and Hydrocarbon Control on Annual Mean NO$_2$ at Lennox

Table 11.3a Percentage Change in Annual Mean NO$_2$

NO$_x$ CONTROL →
(Percentage Changes from 1969-1974 Level)

NMHC CONTROL ↓ (Percentage Changes from 1969-1974 Level)	+20%	0%	-20%	-40%	-60%
+20%	+20%	+1%	-18%	-37%	-56%
0%	+19%	0%	-19%	-38%	-57%
-20%	+18%	-1%	-20%	-39%	-58%
-40%	+17%	-2%	-21%	-40%	-59%
-60%	+16%	-3%	-22%	-41%	-60%

Table 11.3b Annual Mean NO$_2$ Levels, pphm

NO$_x$ CONTROL →
(Percentage Changes from 1969-1974 Level)

NMHC CONTROL ↓ (Percentage Changes from 1969-1974 Level)	+20%	0%	-20%	-40%	-60%
+20%	7.7	6.5	5.3*	4.1*	2.8*
0%	7.7	6.4	5.2*	4.0*	2.8*
-20%	7.6	6.4	5.1*	3.9*	2.7*
-40%	7.5	6.3	5.1*	3.9*	2.6*
-60%	7.6	6.2	5.0*	3.8*	2.6*

*Attains federal standard of 5.3 pphm (100 μg/m^3)

The yearly maximum one-hour NO_2 concentration at Lennox occurs almost invariably in the daytime during the winter. The highest NO_2 concentrations in the winter are approximately 20% greater than summer peaks, and the highest daytime concentrations are about 30% greater than the nighttime peaks. Thus, the control model for peak winter daytime NO_2 represents the control model for yearly maximum NO_2.

The control model for yearly maximum NO_2 is summarized in Table 11.4. This model has been derived by a procedure entirely parallel to the analysis for Downtown Los Angeles (Section 10.4.2). The control model indicates that maximal NO_2 concentrations are slightly less than proportional to NO_x concentrations at Lennox. Moderate improvement in maximal NO_2 can be gained from hydrocarbon control. The benefit of hydrocarbon control on yearly maximum NO_2 appears to be considerably less at Lennox than at Downtown Los Angeles (Tables 10.18 and 10.20).

11.2.2 Azusa, California

The Azusa monitoring site is located about 21 miles ENE of Downtown Los Angeles. Azusa is on the northeast fringe of the area of high emission density which spreads over the central and coastal parts of the Los Angeles region. As such, Azusa can be regarded as a downwind receptor site in the Los Angeles basin.

Table 11.5 summarizes the empirical control model for annual mean NO_2 at Azusa. As was the case with Downtown Los Angeles and Lennox, annual mean NO_2 is essentially proportional to NO_x, with very small benefits resulting from hydrocarbon control. Attaining the federal annual mean standard for NO_2 must depend on NO_x control.

Table 11.4 The Effects of NO_x and Hydrocarbon Control on Yearly Maximum One-Hour NO_2 at Lennox

Table 11.4a Percentage Changes in Yearly Maximum NO_2

NO_x CONTROL →

(Percentage Changes from 1969-1974 Level)

NMHC CONTROL ↓ (Percentage Changes from 1969-1974 Level)

	+20%	0%	-20%	-40%	-60%
+20%	+20%	+4%	-12%	-29%	-45%
0%	+16%	0%	-16%	-32%	-49%
-20%	+12%	-4%	-20%	-36%	-52%
-40%	+8%	-8%	-24%	-40%	-56%
-60%	+5%	-12%	-28%	-44%	-60%

Table 11.4b Yearly Maximum NO_2 Concentrations, pphm

NO_x CONTROL →

(Percentage Changes from 1969-1974 Level)

NMHC CONTROL ↓ (Percentage Changes from 1969-1974 Level)

	+20%	0%	-20%	-40%	-60%
+20%	49	42	36	29	23*
0%	47	41	34	28	21*
-20%	46	39	33	26	19*
-40%	44	38	31	24*	18*
-60%	43	36	29	23*	16*

*Attains the California one-hour standard (25 pphm)

Table 11.5 The Effect of NO_x and Hydrocarbon Control on Annual Mean NO_2 at Azusa

Table 11.5a Percentage Changes in Annual Mean NO_2

NO_x CONTROL →

(Percent Changes from 1969-1974 Level)

↓ NMHC CONTROL (Percentage Changes from 1969-1974 Level)	+20%	0%	-20%	-40%	-60%
+20%	+20%	+1%	-19%	-38%	-57%
0%	+19%	0%	-19%	-39%	-58%
-20%	+19%	-1%	-20%	-40%	-59%
-40%	+18%	-2%	-21%	-40%	-60%
-60%	+17%	-3%	-22%	-41%	-60%

Table 11.5b Annual Mean NO_2 Levels, pphm

NO_x CONTROL →

(Percentage Changes from 1969-1974 Level)

↓ NMHC CONTROL (Percentage Changes from 1969-1974 Level)	+20%	0%	-20%	-40%	-60%
+20%	7.3	6.2	5.0*	3.8*	2.6*
0%	7.3	6.1	4.9*	3.7*	2.6*
-20%	7.2	6.1	4.9*	3.7*	2.5*
-40%	7.2	6.0	4.8*	3.6*	2.5*
-60%	7.1	5.9	4.8*	3.6*	2.4*

*Attains federal standard of 5.3 pphm (100 μg/m^3)

The submodels for annual mean NO_2 at Azusa indicate that the maximum benefit from hydrocarbon control is attained in daytime average NO_2 during the winter. This is consistent with the results for Downtown Los Angeles and Lennox. Nighttime average NO_2 in the summer is also somewhat sensitive to hydrocarbon control. This could mean that oxidant is especially significant to nighttime NO_2 in the case of Azusa; oxidant affects the amount of evening NO converted to NO_2.

Yearly maximum one-hour NO_2 at Azusa invariably occurs during the winter season. The yearly peak is slightly more likely to occur in the nighttime period than in the daytime period. Thus, empirical control models of yearly maximum NO_2 at Azusa were completed for both winter daytime conditions and winter nighttime conditions. These results are presented in Table 11.6.

Table 11.6 indicates that yearly maximum NO_2 in both the daytime and nighttime periods is essentially proportional to NO_x, with moderate effects occurring from hydrocarbon control. The benefit of hydrocarbon control is greater for the daytime peak than for the nighttime peak. For virtually all degrees of control listed in Table 11.6, the yearly maximum will be more likely to occur in the nighttime period than in the daytime period. Thus, the nighttime case (Table 11.6b) is used as the control model for yearly maximum NO_2. Predicted yearly maxima as a function of hydrocarbon and NO_x control are listed in Table 11.7.

11.2.3 Pomona, California

Pomona is located approximately 30 miles east of Downtown Los Angeles. Under the prevailing daytime wind flow, Pomona is downwind of the source-intensive, central/coastal parts of the basin.

Table 11.6 The Effect of NO_x and Hydrocarbon Control on Yearly Maximum NO_2 at Azusa

Table 11.6a Percentage Changes in Winter Daytime Peak

NO_x CONTROL →

(Percentage Changes from 1969-1974 Level)

NMHC CONTROL ↓ (Percentage Changes from 1969-1974 Level)

	+20%	0%	-20%	-40%	-60%
+20%	+26%	+6%	-13%	-33%	-52%
0%	+19%	0%	-19%	-37%	-56%
-20%	+11%	-6%	-24%	-41%	-59%
-40%	+4%	-12%	-29%	-46%	-62%
-60%	-3%	-18%	-34%	-50%	-66%

Table 11.6b Percentage Changes in Winter Nighttime Peak

NO_x CONTROL →

(Percentage Changes from 1969-1974 Level)

NMHC CONTROL ↓ (Percentage Changes from 1969-1974 Level)

	+20%	0%	-20%	-40%	-60%
+20%	+20%	+2%	-16%	-34%	-51%
0%	+17%	0%	-18%	-36%	-54%
-20%	+16%	-2%	-20%	-38%	-56%
-40%	+14%	-4%	-22%	-40%	-58%
-60%	+11%	-7%	-24%	-42%	-60%

Table 11.7. Predicted Yearly Maximum NO_2 Concentrations (pphm) at Azusa as a Function of NO_x and Hydrocarbon Control

NO_x CONTROL →

(Percentage Changes from 1969-1974 Level)

NMHC CONTROL ↓

(Percentage Changes from 1969-1974 Level)

	+20%	0%	-20%	-40%	-60%
+20%	47	40	33	26	19*
0%	46	39	32	25*	18*
-20%	45	38	31	24*	17*
-40%	45	38	31	24*	17*
-60%	44	37	30	23*	16*

*Attains the California one-hour standard (25 pphm)

Table 11.8 presents the empirical control model for annual mean NO_2 at Pomona. Following the pattern at the other Los Angeles sites, annual mean NO_2 at Pomona is almost directly proportional to NO_x control, with slight benefits provided by hydrocarbon control. Again, consistent with the other sites, the submodels indicate that the greatest benefit from hydrocarbon control is accrued in the *daytime* period during the *winter*.

Yearly maximum one-hour NO_2 concentrations at Pomona occur almost invariably in the nighttime period during the winter. Thus, the approprite submodel for yearly maximum NO_2 is the nighttime peak model for the winter. Table 11.9 presents the resulting empirical control model for yearly maximum NO_2 at Pomona. Hydrocarbon control apparently yields significant reductions in the winter nighttime maximum at Pomona and is about two-thirds as important as NO_x control. The regression model indicates that oxidant is an important determinant of the nighttime NO_2 maximum at Pomona. The benefit from hydrocarbon control occurs because hydrocarbon reductions serve to decrease oxidant.

11.2.4 Denver, Colorado

The Denver CAMP site is a "center-city" monitoring site located in downtown Denver. Table 11.10 presents the empirical control model for annual mean NO_2 at the Denver CAMP site. As was the case with the 4 Los Angeles sites, annual mean NO_2 at Denver is approximately proportional to NO_x concentrations. However, contrary to the results for Los Angeles, hydrocarbon control tends to produce slight *increases* in annual mean NO_2 at Denver.

The submodels for average NO_2 at Denver indicate that the main disadvantages from hydrocarbon control occur during the winter (in both the daytime and nighttime periods). At all sites which have been examined,

Table 11.8 The Effect of NO_x and Hydrocarbon Control on Annual Mean NO_2 at Pomona

Table 11.8a Percentage Changes in Annual Mean NO_2

NO_x CONTROL →

(Percentage Changes from 1969-1974 Level)

NMHC CONTROL ↓

(Percentage Changes from 1969-1974 Level)

	+20%	0%	-20%	-40%	-60%
+20%	+21%	+4%	-13%	-30%	-47%
0%	+17%	0%	-17%	-34%	-51%
-20%	+12%	-4%	-21%	-38%	-54%
-40%	+8%	-9%	-25%	-41%	-58%
-60%	+3%	-13%	-30%	-45%	-61%

Table 11.8b Annual Mean NO_2 Levels, pphm

NO_x CONTROL →

(Percentage Changes from 1969-1974 Level)

NMHC CONTROL ↓

(Percentage Changes from 1969-1974 Level)

	+20%	0%	-20%	-40%	-60%
+20%	9.2	7.9	6.6	5.3*	4.0*
0%	8.8	7.6	6.3	5.0*	3.7*
-20%	8.5	7.2	6.0	4.7*	3.5*
-40%	8.2	6.9	5.7	4.4*	3.2*
-60%	7.8	6.6	5.4	4.1*	2.9*

*Attains federal annual mean standard of 5.3 pphm (100 μg/m^3)

Table 11.9 The Effect of NO_x and Hydrocarbon Control on Yearly Maximum NO_2 at Pomona

Table 11.9a Percentage Changes in Yearly Maximum NO_2

NO_x CONTROL →

(Percentage Changes from 1969-1974 Level)

NMHC CONTROL ↓

(Percentage Changes from 1969-1974 Level)

	+20%	0%	-20%	-40%	-60%
+20%	+20%	+8%	-5%	-17%	-30%
0%	+12%	0%	-12%	-25%	-37%
-20%	+5%	-8%	-20%	-32%	-45%
-40%	-3%	-15%	-28%	-40%	-52%
-60%	-11%	-23%	-35%	-48%	-60%

Table 11.9b Yearly Maximum NO_2 Concentrations, pphm

NO_x CONTROL →

(Percentage Changes from 1969-1974 Level)

NMHC CONTROL ↓

(Percentage Changes from 1969-1974 Level)

	+20%	0%	-20%	-40%	-60%
+20%	49	44	39	34	29
0%	46	41	35	30	25*
-20%	42	37	32	27	22*
-40%	39	34	29	24*	19*
-60%	36	31	26	21*	16*

*Attains the California one-hour standard of 25 pphm

Table 11.10 The Effect of NO_x and Hydrocarbon Control on Annual Mean NO_2 at Denver

Table 11.10a Percentage Changes in Annual Mean NO_2 Levels

NO_x CONTROL →

(Percentage Changes from 1969-1974 Level)

NMHC CONTROL ↓

(Percentage Changes from 1969-1974 Level)

	+20%	0%	-20%	-40%	-60%
+20%	+19%	-3%	-24%	-46%	-68%
0%	+21%	0%	-22%	-44%	-66%
-20%	+23%	+2%	-20%	-42%	-64%
-40%	+26%	+4%	-18%	-40%	-62%
-60%	+28%	+6%	-16%	-38%	-60%

Table 11.10b Annual Mean NO_2 Concentrations, pphm

NO_x CONTROL →

(Percentage Changes from 1969-1974 Level)

NMHC CONTROL ↓

(Percentage Changes from 1969-1974 Level)

	+20%	0%	-20%	-40%	-60%
+20%	4.6*	3.7*	2.9*	2.1*	1.2*
0%	4.6*	3.8*	3.0*	2.1*	1.3*
-20%	4.7*	3.9*	3.1*	2.2*	1.4*
-40%	4.8*	4.0*	3.2*	2.3*	1.5*
-60%	4.9*	4.1*	3.2*	2.4*	1.5*

*All values attain federal annual mean standard of 5.3 pphm (100 $\mu g/m^3$)

it was found that hydrocarbon reductions tend to increase afternoon NO_2. This effect appears to be especially important at Denver during the winter. The increased afternoon NO_2 leads to increases in both daytime average NO_2 and nighttime average NO_2 at Denver.

As was the case with Downtown Los Angeles and Lennox, yearly one-hour maximum NO_2 at Denver invariably occurs in the daytime period during the winter. Table 11.11 presents the empirical control model for yearly maximum NO_2 at Denver. It is evident that yearly maximum NO_2 is nearly proportional to NO_x and that hydrocarbon control yields slight to moderate benefits.

It is interesting to note that, at Denver in the winter, hydrocarbon control reduces daytime peak NO_2 levels but increases daytime average NO_2 levels. The increase in afternoon NO_2 from hydrocarbon control evidently more than compensates for the reduction in peak morning concentrations. On the contrary, at the Los Angeles sites, the reduction in daytime peak NO_2 affects the daytime average more than the increase in afternoon NO_2 concentrations.

11.2.5 Chicago, Illinois

The Chicago CAMP site is a "center-city" monitoring location located in the southeast part of Chicago. Table 11.12 presents the empirical control model for annual mean NO_2 at Chicago. The model indicates that annual mean NO_2 in Chicago is directly proportional to NO_x control and independent of hydrocarbon control.

Table 11.11 The Effect of NO_x and Hydrocarbon Control on Yearly Maximum NO_2 at Denver

Table 11.11a Percentage Changes in Yearly Maximum NO_2

NO_x CONTROL →

(Percentage Changes from 1969-1974 Level)

NMHC CONTROL ↓

(Percentage Changes from 1969-1974 Level)

	+20%	0%	-20%	-40%	-60%
+20%	+20%	+3%	-14%	-31%	-48%
0%	+17%	0%	-17%	-34%	-51%
-20%	+14%	-3%	-20%	-37%	-54%
-40%	+11%	-6%	-23%	-40%	-57%
-60%	+8%	-9%	-26%	-43%	-60%

Table 11.11b Yearly Maximum NO_2 Concentrations, pphm

NO_x CONTROL →

(Percentage Changes from 1969-1974 Level)

NMHC CONTROL ↓

(Percentage Changes from 1969-1974 Level)

	+20%	0%	-20%	-40%	-60%
+20%	44	38	31	25	19
0%	43	37	30	24	18
-20%	42	36	29	23	17
-40%	41	34	28	22	16
-60%	40	33	27	21	15

Table 11.12 The Effect of NO_x and Hydrocarbon Control on Annual Mean NO_2 at Chicago

Table 11.12a Percentage Changes in Annual Mean NO_2

NO_x CONTROL →

(Percentage Changes from 1969-1974 Level)

NMHC CONTROL ↓

(Percentage Changes from 1969-1974 Level)

	+20%	0%	-20%	-40%	-60%
+20%	+20%	0%	-20%	-40%	-60%
0%	+20%	0%	-20%	-40%	-60%
-20%	+20%	0%	-20%	-40%	-60%
-40%	+20%	0%	-20%	-40%	-60%
-60%	+20%	0%	-20%	-40%	-60%

Table 11.12b Annual Mean NO_2 Concentrations, pphm

NO_x CONTROL →

(Percentage Changes from 1969-1974 Level)

NMHC CONTROL ↓

(Percentage Changes from 1969-1974 Level)

	+20%	0%	-20%	-40%	-60%
+20%	6.9	5.8	4.6*	3.4*	2.3*
0%	6.9	5.8	4.6*	3.4*	2.3*
-20%	6.9	5.8	4.6*	3.4*	2.3*
-40%	6.9	5.8	4.6*	3.4*	2.3*
-60%	6.9	5.8	4.6*	3.4*	2.3*

*Attains federal annual mean standard of 5.3 pphm (100 $\mu g/m^3$)

The submodels for annual mean NO_2 indicate that hydrocarbon control does yield a modest benefit in daytime NO_2 averages during the winter. However, this benefit is almost exactly cancelled by an increase in nighttime NO_2 averages (in both summer and winter). NO_2 levels at night are increased by hydrocarbon control because hydrocarbon reductions lead to greater levels of NO_2 in the afternoon.

Unlike Denver and the Los Angeles sites, yearly maximum NO_2 in Chicago will almost always occur in the summer during the daytime period. The statistical models for peak NO_2 in the summer at Chicago indicated that there was no statistically significant effect from hydrocarbons. Thus, yearly maximum NO_2 at Chicago should be directly proportional to NO_x control and independent of hydrocarbon control (see Table 11.13).

11.2.6 Houston/Mae, Texas

The Mae Drive site is located about two miles north of the Houston Ship Channel, immediately downwind of the large, heavily industrialized area that surrounds the channel. The Mae Drive station can be considered representative of air quality near a source-intensive area.

As indicated by the regression results in Appendix D, the Houston sites (Aldine as well as Mae) were unique among all the sites studied in the sense that a significant dependence between daytime NO_2 and hydrocarbons was never found, neither for peak NO_2 nor for average NO_2, neither during winter nor during summer. One reason for this result might be the sparsity of available data for the Houston sites, typically about 60 to 90 days for each season as compared to 300 to 700 days for each season at CAMP sites and Los Angeles sites. There may have been

Table 11.13 The Effects of Hydrocarbon Control on Yearly Maximum One-Hour NO_2 at Chicago

Table 11.13a Percentage Changes in Yearly Maximum NO_2

NO_x CONTROL ⟶

(Percentage Changes from 1969-1974 Level)

NMHC CONTROL ⟶ (Percentage Changes from 1969-1974 Level)

	+20%	0%	-20%	-40%	-60%
+20%	+20%	0%	-20%	-40%	-60%
0%	+20%	0%	-20%	-40%	-60%
-20%	+20%	0%	-20%	-40%	-60%
-40%	+20%	0%	-20%	-40%	-60%
-60%	+20%	0%	-20%	-40%	-60%

Table 11.13b Yearly Maximum One-Hour Concentrations, pphm

NO_x CONTROL ⟶

(Percentage Changes from 1969-1974 Level)

NMHC CONTROL ⟶ (Percentage Changes from 1969-1974 Level)

	+20%	0%	-20%	-40%	-60%
+20%	30	25	20	15	10
0%	30	25	20	15	10
-20%	30	25	20	15	10
-40%	30	25	20	15	10
-60%	30	25	20	15	10

insufficient data for the regressions to arrive at statistically significant hydrocarbon coefficients. The other reason would be that no hydrocarbon effect actually exists for daytime NO_2 in Houston. This possibility is reasonable because the $NMHC/NO_x$ ratio at Houston is quite high (around 15 to 20), and because photochemical systems tend to be less sensitive to hydrocarbon control at high $NMHC/NO_x$ ratios.

The nighttime regressions for Houston/Mae revealed a significant relationship between afternoon oxidant and nighttime NO_2. However, we were hesitant to translate the nighttime NO_2/oxidant dependence into a control model. The reason for caution is that the nighttime model requires an assumed relationship between oxidant and the primary pollutants, NMHC and NO_x. For the Los Angeles and CAMP sites, we had assumed that oxidant would be proportional to the $NMHC/NO_x$ ratio. This assumption would be more dubious for Houston because investigations have shown little relationship between NMHC and oxidant at Houston[1]. The high ambient $NMHC/NO_x$ ratio at Houston also lends doubt concerning the effectiveness of small-to-moderate hydrocarbon reductions on oxidant in Houston.

Fortunately, our calculations demonstrated that the control model for annual mean NO_2 is insensitive to the assumed relationship between oxidant and precursors. Regardless of what assumption is adopted, the control model indicates that annual mean NO_2 is essentially proportional to NO_x control, with very slight changes produced by hydrocarbon control. For instance, if we assume that afternoon oxidant is proportional to the NMHC/NO_x ratio, the control model would indicate that a 50% hydrocarbon reduction produces only a 6% decrease in annual mean NO_2. If we made a very different assumption, that afternoon oxidant is proportional to NO_x and independent of hydrocarbons, the control model would indicate that a 50% hydrocarbon reduction produces a 1% increase in annual mean NO_2.

From the above considerations, we conclude that a control model such as Table 11.12a (in the Chicago discussion), where annual mean NO_2 is proportional to NO_x and independent of hydrocarbons, is a good approximation for Houston/Mae. The present (1975-1976) level of annual mean NO_2 at Houston/Mae is 2.5 pphm. Managing annual mean NO_2 air quality at Houston/Mae should depend on strategies for NO_x emissions only.

The yearly maximum one-hour NO_2 concentration at Houston/Mae is approximately 13 pphm. The yearly NO_2 maximum is most likely to occur in the winter season, but is equally likely to occur during the daytime and nighttime periods. The daytime regression equations (Appendix D) indicate that the winter daytime NO_2 peak at Houston/Mae will be proportional to NO_x control and independent of hydrocarbon control. Thus a control model such as Table 11.13a is appropriate for the daytime yearly maximum at Houston/Mae.

Calculations based on the nighttime regressions reveal that the winter nighttime peak NO_2 at Houston/Mae will be as sensitive to oxidant control as to NO_x control. Since we are unsure of the relationship between oxidant and primary precursors in Houston, we have not constructed an empirical control model relating the winter nighttime NO_2 peak to the primary precursors. It suffices to note that a strategy for reducing oxidant at Houston/Mae should also yield substantial benefits in terms of nighttime yearly peak NO_2. Our calculations show that a 50% reduction in oxidant (with constant NO_x) would produce a 30% reduction in the nighttime yearly maximum NO_2 concentration at Houston/Mae.

11.2.7 Houston/Aldine, Texas

The Houston/Aldine monitoring site is located about 12 miles north of downtown Houston and about 13 miles northeast of the Houston Ship Channel. Since the dominant wind direction is from the southeast, the Aldine site can be regarded as a receptor location, about 12 to 13 miles downwind of the main source areas in Houston.

As was the case with the Mae Drive site, the daytime regressions for Houston/Aldine revealed no significant relationships between daytime NO_2 (peak or average) and NMHC concentrations. The lack of a statistically significant hydrocarbon effect could be due to the sparsity of data at the Houston sites. The other possibility is that no hydrocarbon effect actually exists for daytime NO_2 in Houston.

The nighttime regression models for Houston/Aldine did not provide good statistical fits to the data. The winter nighttime regressions achieved a correlation coefficient of less than 0.6, and the summer nighttime regressions failed to produce any statistically significant relationships between nighttime NO_2 and the "independent" variables: afternoon NO_2 ($NO_2$16), evening NO (NITENO), and afternoon ozone (O_3AFT).

The failure of the nighttime regression models at Aldine most likely results because of the neglect of transport. Contacts with personnel of the Texas Air Control Board [2] indicate that the elevated nighttime NO_2 concentrations at Aldine most likely result from pollution transport from the upwind source areas. Evidence of transport is demonstrated in Figure 9.12, which shows that NO_2, NO_x, and NMHC concentrations simultaneously jump upwards at about 7:00 PM. This could be due to the arrival of afternoon industrial emissions and evening traffic emissions transported to the Aldine site. The persistence of high oxidant levels as late as 6:00 P.M. (see Figure 9.12) is also evidence of transport. Since the empirical models are based on the assumption that transport is not a dominant factor, the models may be inappropriate for the Houston/Aldine location.*

The failure of the statistical approach in the case of nighttime NO_2 at Aldine precludes our formulating an empirical control model for annual mean NO_2 at Aldine; a control model for annual mean NO_2 would require submodels for both the daytime and nighttime periods. Also, since yearly maximal NO_2 concentrations at Aldine invariably occur during the nighttime period, we cannot formulate an empirical control model for peak one-hour NO_2 at Aldine.**

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*Note that the results for Aldine also place doubt on our models for Azusa and Pomona in Los Angeles. Azusa and Pomona are downwind receptor locations, and they exhibit diurnal patterns similar to Aldine (although not as extreme). In the next chapter, it will be shown that the control models for Azusa and Pomona are not verified by historical air quality trends. The neglect of transport may be inappropriate for Azusa and Pomona as well as for Aldine.

**For reference, the reader may wish to note that the present annual mean NO_2 concentration at Aldine is 1.70 pphm. The yearly one-hour maximum is 11 pphm and occurs during the winter nighttime period.

11.3 REFERENCES

1. G. K. Tannahill, "The Hydrocarbon/Ozone Relationship in Texas," presented at the Air Pollution Control Association Conference on Ozone/Oxidants, Texas Air Control Board, Dallas, March 1976.
2. J. Price and T. Echols, Air Quality Evaluation Division of the Texas Air Control Board, personal communication, May 1977.

12.0 VALIDATION OF EMPIRICAL MODELS AGAINST HISTORICAL AIR QUALITY TRENDS

The empirical NO_2 control models developed in this report are subject to several limitations: the omission of meteorological variables, the neglect of transport phenomena, and the assumption that precursor changes produced by variance in meteorology can be used to model the effect of control strategies. The uncertainties in the models were highlighted in Chapter 10, where analyses with weather variables indicated that the observed effect of hydrocarbons on NO_2 might partially be due to unaccounted for meteorological factors. These uncertainties stress the need to conduct independent checks of the empirical control models. Accordingly, this chapter checks the predictions of the models against historical air quality trends.

Although the empirical models and the historical trends are both based on ambient data, the trend studies do provide an independent validation of the models. For one, the trend studies employ several more years of data than the empirical models. Also, the trend studies are based on year-to-year changes in precursors and NO_2, while the empirical models are based on day-to-day changes in precursors and NO_2.

The procedure for validating the empirical models is quite simple. First, best estimates of historical precursor changes are derived based on emission trend data and ambient trend data for NO_x and NMHC. Next, these historical precursor changes are entered into the control models to predict historical NO_2 trends. Finally, the predicted trends for NO_2 are compared with actual trends for NO_2.

The validation studies will be conducted for 5 locations: the central Los Angeles area, coastal Los Angeles area, inland Los Angeles area, Denver, and Chicago. The empirical control models for Houston cannot be checked against historical trends because of the lack of long-term data for the Houston sites.

12.1 CENTRAL LOS ANGELES AREA

This section tests the empirical control model for Downtown Los Angeles against historical air quality trends. To provide generality in the test, the verification is performed for 3 locations in the central part of the Los Angeles basin: Downtown Los Angeles (DOLA), Burbank, and Reseda. The verification proceeds in two steps. First, net changes in precursor (NO_x and NMHC) levels are estimated over the nine years, 1965 to 1974. Second, the precursor trends are entered into the control model, and the resulting predictions of NO_2 changes are compared with actual NO_2 trends.

12.1.1 Precursor Trends, 1965-1974

Two types of data can be used to estimate trends in photochemical precursors: emission data and ambient precursor data. Both are examined below to arrive at "best estimates" of precursor trends at DOLA, Burbank, and Reseda.

Emission Trends

A recent report of the Caltech Environmental Quality Laboratory provides emission trend data for the Los Angeles region [1]. Figures 12.1 and 12.2 summarize the EQL estimates of basin-wide emission trends for NO_x and RHC, respectively. Basin-wide NO_x emissions increased by 35% from 1965 to 1974, while basin-wide RHC emissions decreased by 18%. Nearly all of the NO_x

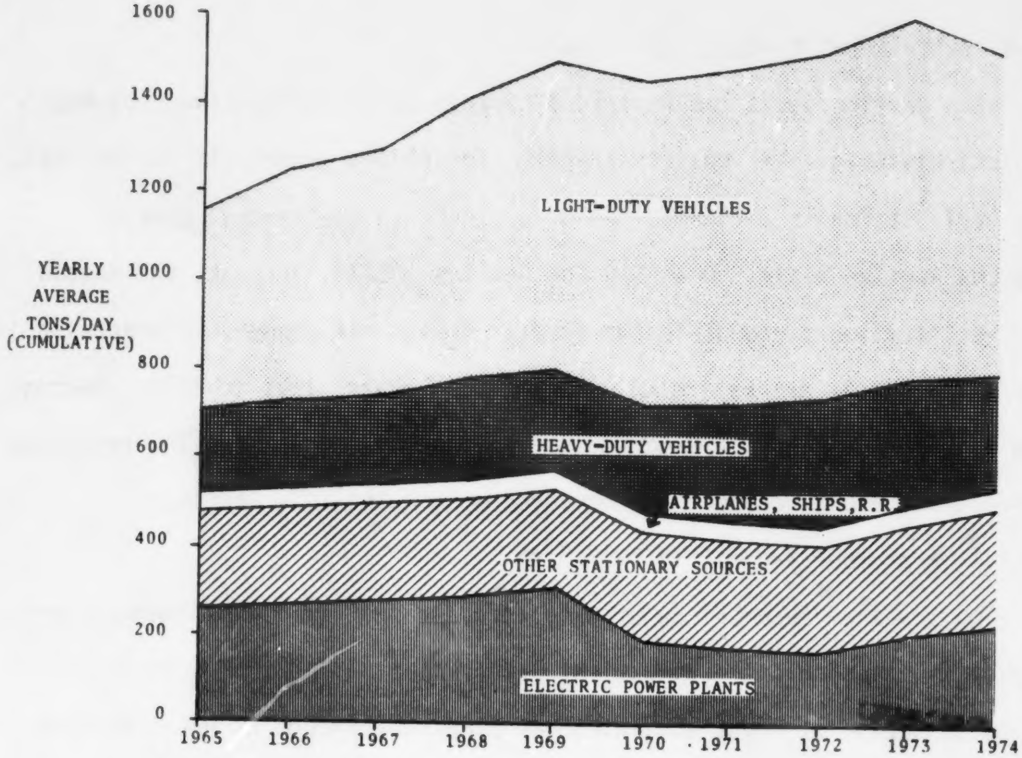

Figure 12.1 Total NO_x Emission Trends in the Los Angeles Basin[1]

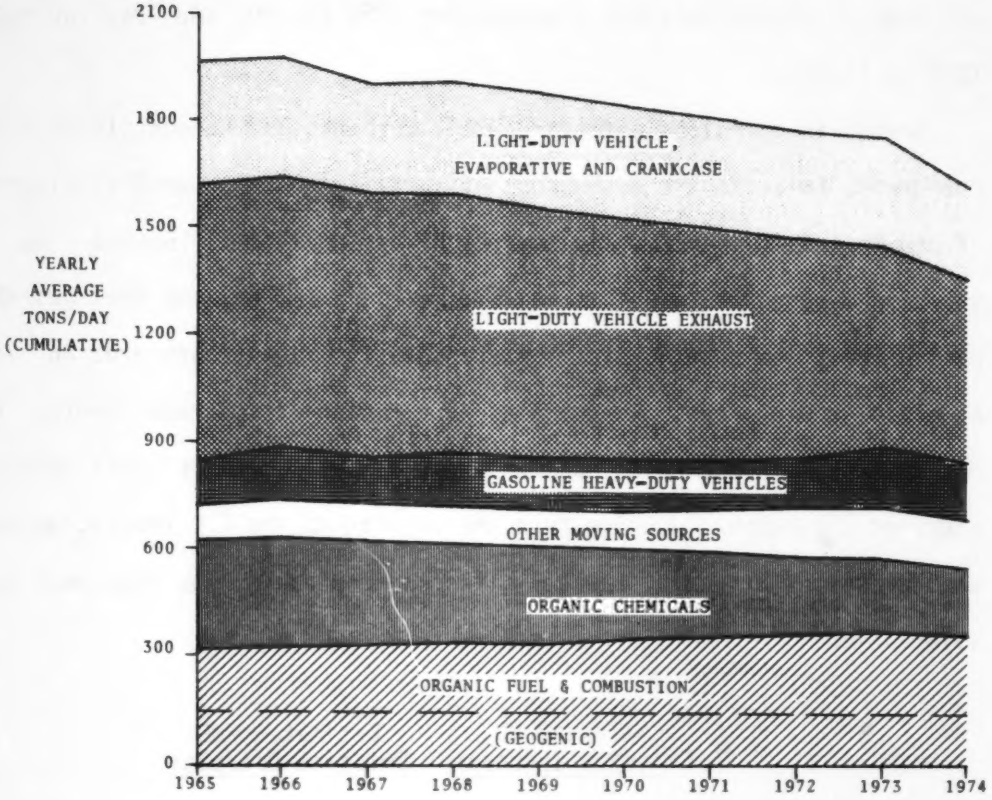

Figure 12.2 Total Reactive Hydrocarbon Emission Trends in the Los Angeles Basin[1]

increase and the RHC decrease resulted from changes in emissions from gasoline-powered motor vehicles.

The EQL report also documents emission trends on a county-by-county basis. Because of low growth rates in Los Angeles County (see Figure 12.3), Los Angeles County emissions decreased relative to the basin-wide total emissions. Los Angeles County emission changes were +25% for NO_x and -24% for RHC from 1965 to 1974[1].

Trends in emissions affecting DOLA, Burbank, and Reseda differ from countywide emission trends because of variations in the spatial distribution of growth and in the specific sources affecting those 3 locales. As shown in Figure 12.3, DOLA is in (and downwind of) an area that has exhibited particularly low growth rates. Burbank is in a low-growth area but is near moderate-growth areas. Reseda lies in a region of moderate growth. Estimating trends in the emissions that affect these specific sites requires educated guesswork. Judging from the results of the EQL report, we estimate that emissions affecting these 3 sites changed as follows from 1965 to 1974:

	Estimated NO_x Emission Increase	Estimated RHC Emission Decrease
DOLA	10%-20%	30%-40%
Burbank	15%-25%	25%-35%
Reseda	25%-35%	15%-25%

Ambient NO_x Trends

An alternative method of estimating precursor trends is to examine ambient data. To minimize statistical fluctuations in the trend estimates,

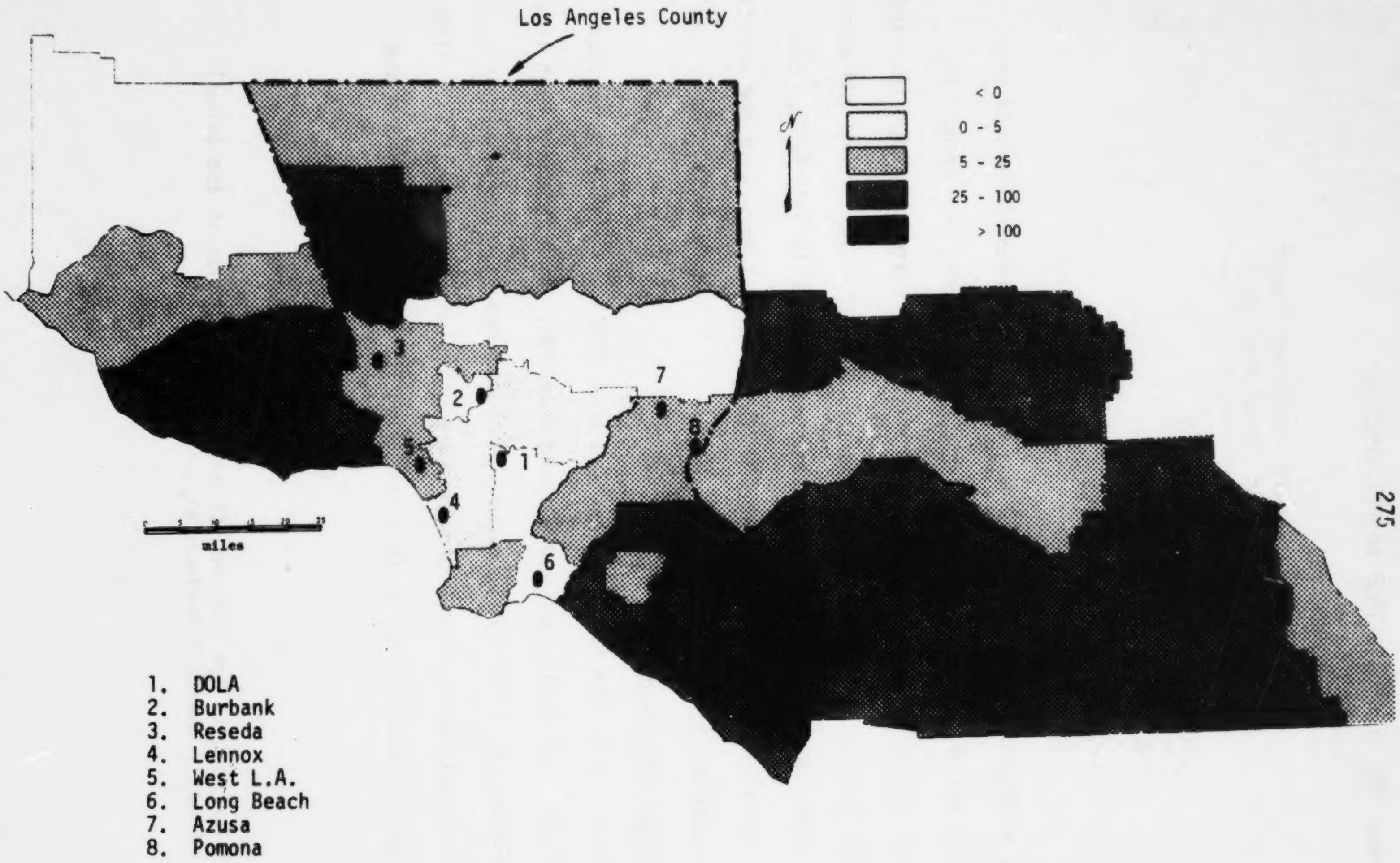
Los Angeles County
< 0
0 - 5
5 - 25
25 - 100
> 100
N
miles
1
2
3
4
5
6
7
8
1. DOLA
2. Burbank
3. Reseda
4. Lennox
5. West L.A.
6. Long Beach
7. Azusa
8. Pomona

Figure 12.3 Geographical Distribution of Percentage Change in Population in the Los Angeles Basin, 1965 to 1975 [2]

a large sample of air quality data should be used. The net changes in ambient NO_x listed below are based on changes in three-year averages of annual mean NO_x from 1964-1966 to 1973-1975[3]:

	Net Nine-Year Change in Annual Mean NO_x*
DOLA	+ 1%
Burbank	+ 7%
Reseda	+31%

The nine-year change in ambient NO_x at Reseda agrees quite well with the estimated NO_x emission change for Reseda. However, the ambient NO_x increases at DOLA and Burbank are less than the estimated emission increases for those sites. Part of the discrepancy between emission trends and ambient trends might be due to low air pollution potential in 1973-1975[2]. Some of the discrepancy might also arise from the potential errors in the emission trend estimates for DOLA and Burbank.

Ambient NMHC Trends

Ambient trend data for total hydrocarbons (THC) are available at DOLA and Burbank. Estimating long-term changes in NMHC concentrations with this data, however, is a tenuous procedure. Ambient hydrocarbon measurements are considerably more error-prone than are other monitoring data[4]. Also, conceptual difficulties arise in translating THC trends into NMHC trends.

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*Similar results are obtained if one examines trends in the annual average of daily one-hour maximum NO_x.

Using a very simple procedure to calculate NMHC levels from THC levels,* approximate estimates of ambient NMHC trends can be derived. The resulting estimates of nine-year changes in ambient NMHC concentrations are as follows[3]:

	Net Nine-Year Change in Annual Mean NMHC
DOLA	-42%
Burbank	- 8%

The ambient NMHC trends at DOLA agree with the estimates of RHC emission trends, but the ambient NMHC reductions at Burbank are significantly less than the estimated RHC emission reductions. The discrepancy at Burbank most likely arises from errors in the ambient trends. In particular, the reader should note that hydrocarbon monitoring at Burbank was discontinued from 1966 to 1969[3].

Best Estimates of Precursor Trends

By considering both emission trend data and ambient trend data, one can arrive at reasonable estimates of precursor changes at DOLA, Burbank, and Reseda. In deriving best estimates of NO_x trends, emphasis should be placed on ambient data, because the ambient trends best represent overall changes in emissions affecting each location. Because of uncertainties in ambient hydrocarbon trends, emission data should be given greater weight in the case of hydrocarbons.

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*NMHC trends are estimated from THC trends, using the relation NMHC = (THC-1ppm)/2 (see Chapter 10). The accuracy of this formula changes as relative THC and NMHC levels alter with time. This leads to a basic conceptual difficulty in estimating NMHC trends from THC trends.

Table 12.1 presents our best estimates of NO_x and NMHC trends from 1965 to 1974 at the 3 central Los Angeles basin locations. The estimates are rounded to the nearest 5%. Also presented are approximate error bounds; these are based on subjective analysis of the uncertainties.

Table 12.1 Best Estimates of Nine-Year NO_x and NMHC Trends at DOLA, Burbank, and Reseda

Station	NO_x Change 1965-1974	NMHC Change 1965-1974
DOLA	+ 5% ± 5%	-40% ± 10%
Burbank	+10% ± 5%	-25% ± 10%
Reseda	+30% ± 5%	-20% ± 10%

12.1.2 Test of the Empirical Control Model

The empirical NO_2 control models for DOLA can be tested against historical air quality trends at DOLA, Burbank, and Reseda. The procedure is very simple. The NO_x and NMHC trends in Table 12.1 are entered into the control models, Table 10.16a for annual mean NO_2 and Table 10.18 for yearly maximum NO_2.* The resulting predictions are then compared with actual changes in NO_2 concentrations from 1965 to 1974.

Table 12.2 presents the verification test for annual mean NO_2. The actual and predicted changes in annual mean NO_2 are almost exactly equal at DOLA and Reseda and are off 5 percentage points at Burbank.

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*Tables 10.16a and 10.18 present only values up to a +20% NO_x change. The tables were extended to greater NO_x changes in order to test the model at Reseda.

Table 12.2 Test of DOLA Empirical Control Model for Annual Mean NO_2

Station	Precursor Changes, 1965-1974 NO_x	RHC	Predicted Nine-Year Change in Annual Mean NO_2 Conc.	Actual Nine-Year Change in Annual Mean NO_2 Conc.*
DOLA	+ 5%	-40%	0%	+ 1%
Burbank	+10%	-25%	+ 7%	+12%
Reseda	+30%	-20%	+25%	+23%
Average	+15%	-28%	+11%	+12%

Table 12.3 presents the verification test for yearly one-hour maximal NO_2 concentrations. The 99th percentile of daily one-hour maximum NO_2 is also used in the test, because this air quality index is subject to less statistical noise than the single yearly maximum value. The agreement at DOLA and Reseda is again very good. The discrepancy between actual and predicted changes at Burbank is 9 percentage points.

Table 12.3 Test of DOLA Empirical Control Model for Yearly Maximum One-Hour NO_2

Station	Precursor Changes 1965-1974		Predicted Nine-Year Change in Yearly One-Hour Max. NO_2	Actual Nine-Year NO_2 Conc. Changes*	
	NO_x	RHC		Yearly One-Hour Max.	99th Percentile of Daily Max.
DOLA	+ 5%	-40%	-17%	-19%	- 7%
Burbank	+10%	-25%	- 6%	+ 3%	+ 3%
Reseda	+30%	-20%	+11%	+19%	+ 9%
Average	+15%	-28%	- 4%	+ 1%	+ 2%

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*Change in three-year average 1964-1966 to 1973-1975

In a qualitative sense, the test of the DOLA empirical control model is extremely encouraging. The control model predicts that hydrocarbon reductions should decrease yearly maximum NO_2 relative to yearly average NO_2; this effect has occurred at all 3 monitoring sites (see actual trends in Tables 12.2 and 12.3). It is also encouraging that the models for both annual mean NO_2 and yearly maximum NO_2 exhibit good quantitative accuracy at DOLA and Reseda.

12.2 COASTAL LOS ANGELES AREA

This section tests the empirical control model for Lennox against historical air quality trends. The test is performed for 3 coastal locations: Lennox, Long Beach, and West Los Angeles.

12.2.1 Precursor Trends, 1965-1974

The first part of the verification study is to determine historical precursor trends from 1965-1974. Below, both emission data and ambient precursor data are used to arrive at "best estimates" of precursor trends at the 3 coastal locations.

Emission Trends

Trends in emissions which affect Lennox, Long Beach, and West Los Angeles can be estimated by considering the results of the EQL trend study [1], the source mix near the areas [5], and the growth patterns within the Los Angeles region (Figure 2.3). Our estimates of emission changes from 1965 to 1974 are as follows:

	Estimated NO_x Emission Increase	Estimated RHC Emission Decrease
Lennox	5% - 15%	20% - 30%
Long Beach	0% - 10%	25% - 35%
West Los Angeles	20% - 30%	20% - 30%

Ambient NO_x Trends

Trends in ambient NO_x are determined by examining changes in three-year averages of annual mean NO_x, from 1964-1966 to 1973-1975. These changes are as follows:

	Net Nine-Year Change in Annual Mean NO_x
Lennox	+5%
Long Beach	-16%
West Los Angeles	+9%

For all 3 sites, ambient NO_x increased less than the estimated change in NO_x emissions. Some of this discrepancy may be due to more favorable meteorology in 1973-1975[2]. Also, it should be noted that, for these 3 sites, slightly more positive trends for ambient NO_x are obtained using three-year averages of daily peak NO_x rather than three-year averages of annual mean NO_x.

Ambient NMHC Trends

Data on ambient hydrocarbon trends at coastal sites in Los Angeles are available only at Lennox, and only for the years 1970-1975 [3]. For those years, the decrease in NMHC concentrations* at Lennox appears to be about one-half of the decrease in NMHC at DOLA. Using the nine-year trends at DOLA, extrapolation indicates that the net nine-year change at Lennox (1965 to 1974) was a decrease of 20%. This estimate of ambient NMHC trends at Lennox agrees fairly well with the estimated RHC emission change.

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*NMHC concentrations are estimated from THC concentrations as explained previously.

Best Estimates of Precursor Trends

Table 12.4 presents our best estimates of NO_x and NMHC trends from 1965 to 1974 at the 3 coastal locations. In obtaining these best estimates, ambient data were given the greatest weight for NO_x, and emission data were given the greatest weight for NMHC. Again, approximate error bounds are specified based on a subjective analysis of the uncertainties.

Table 12.4 Best Estimates of Nine-Year NO_x and NMHC Trends at Lennox, Long Beach, and West LA

Station	NO_x Change 1965-1974	NMHC Change 1965-1974
Lennox	+5% ± 5%	-25% ± 10%
Long Beach	-10% ± 10%	-30% ± 10%
West LA	+15% ± 5%	-25% ± 10%

12.2.2 Test of the Empirical Control Model

To test the empirical control model for Lennox, the NO_x and NMHC trends in Table 12.4 are entered into Tables 11.3a and 11.4a. The resulting predictions are then compared with actual trends in NO_2 concentrations from 1965 to 1974.

Table 12.5 presents the test for annual mean NO_2. The agreement between actual and predicted is good at Lennox, fair at West LA, and poor at Long Beach. The discrepancies at West LA and Long Beach could be due to errors in the precursor trend estimates for those sites.

Table 12.5 Test of Lennox Empirical Control Model for Annual Mean NO_2

Station	Precursor Changes 1965-1974		Predicted Nine-Year Change in Annual Mean NO_2 Conc.	Actual Nine-Year Change in Annual Mean NO_2 Conc.
	NO_x	RHC		
Lennox	+5%	-25%	+3%	-1%
Long Beach	-10%	-30%	-11%	+10%
West LA	+15%	-25%	+13%	+22%
Average	+3%	-27%	+2%	+10%

Table 12.6 presents the test for yearly one-hour maximal NO_2. The agreement at Lennox is good. The agreement at Long Beach and West LA is very sensitive to which air quality index is used to measure actual trends in maximal NO_2 concentrations. The statistical noise in the actual trends is quite large for maximal concentrations because they are based on few observations.

Table 12.6 Test of Lennox Control Model for Yearly Maximum One-Hour NO_2

Station	Precursor Changes 1965-1974		Predicted Nine-Year Change in Yearly One-Hour Max. NO_2	Actual Nine-Year Conc. Changes	
	NO_x	RHC		Yearly One-Hour Max.	99th Percentile of Daily Max.
Lennox	+5%	-25%	-1%	-3%	+1%
Long Beach	-10%	-30%	-14%	-20%	+1%
West LA	+15%	-25%	+7%	+31%	+6%
Average	+3%	-27%	-3%	+3%	+3%

Again, in a qualitative sense, the verification study is encouraging. The control model predicts that hydrocarbon control should reduce maximum

NO_2 relative to yearly average NO_2. This effect is apparent in the actual NO_2 trends, especially if the actual trends are averaged over the 3 locations.

12.3 INLAND LOS ANGELES AREA

Empirical control models have been formulated for two eastern/inland sites in the Los Angeles basin--Azusa and Pomona. This section tests those models against historical air quality trends.

12.3.1 Precursor Trends, 1965-1974

Estimates of historical precursor trends are required to test the control models. Both emission data and ambient data are used to arrive at "best estimates" of precursor trends at Azusa and Pomona.

Emission Trends

Azusa and Pomona are located in areas of moderate-to-high growth rates (see Figure 2.3). Considering the growth rate of sources near those areas and the results of the EQL study [1], we estimate that emissions affecting Azusa and Pomona changed as follows from 1965 to 1974:

	Estimated NO_x Emission Increase	Estimated RHC Emission Decrease
Azusa	25%- 35%	15%- 25%
Pomona	25%- 35%	15%- 25%

Ambient NO_x Trends

Trends in ambient NO_x are determined by examining changes in three-year averages of annual mean NO_x from 1964-1965 to 1973-1974. These results are as follows:

	Net Nine-Year Change in Annual Mean NO_x
Azusa	+46%
Pomona	+25%

Similar results would be obtained if yearly averages of daily maximum one-hour NO_x were used instead of annual mean NO_x concentrations.

Ambient NMHC Trends

Ambient hydrocarbon data are available at Azusa for the entire ten-year period. Estimated NMHC trends at Azusa are a 41% increase or an 11% increase, using annual mean concentrations and yearly average of daily maximum concentrations, respectively. The increase in ambient hydrocarbons directly contradicts the estimated decrease in RHC emissions. Most of the discrepancy probably arises from potential errors in determining ambient NMHC trends.

Best Estimates of Precursor Trends

Table 12.7 presents our best estimates of nine-year trends in precursors affecting Azusa and Pomona. Ambient data were again given the greatest weight for NO_x, while emission estimates were given greatest emphasis for NMHC. There is a large error bound on the hydrocarbon trend estimates because of the discrepancy between RHC emission trend estimates and ambient NMHC changes at Azusa.

Table 12.7 Best Estimates of Nine-Year NO_x and NMHC Trends at Azusa and Pomona

Station	NO_x Change 1965-1974	NMHC Change 1965-1974
Azusa	+40% ± 5%	-10% ± 15%
Pomona	+25% ± 5%	-15% ± 15%

12.3.2 Test of the Empirical Control Models

The empirical control models for Azusa and Pomona are tested by entering the precursor trends in Table 12.7 into the control models (Tables 11.6 through 11.9[*]). The resulting predictions of ambient NO_2 trends are then compared with actual NO_2 changes from 1965 to 1974.

Table 12.8 presents the test for annual mean NO_2. The agreement is good at both Azusa and Pomona. It is interesting to note that the empirical model for Pomona indicates a larger hydrocarbon effect than the empirical model for Azusa, and that this agrees with the relative long-term trends in annual mean NO_2.

Table 12.8 Test of Azusa and Pomona Control Models for Annual Mean NO_2

Station	Precursor Changes 1965-1974 NO_x	RHC	Predicted Nine-Year Change in Annual Mean NO_2 Conc.	Actual Nine-Year Change in Annual Mean NO_2 Conc.
Azusa	+40%	-10%	+39%	+37%
Pomona	+25%	-15%	+17%	+11%
Average	+33%	-13%	+28%	+24%

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[*] Tables 11.6 and 11.9 were extended to account for the large NO_x increases at Azusa and Pomona.

Table 12.9 presents the verification test for yearly one-hour maximum NO_2. The agreement between the model predictions and the actual trends in the 99th percentile of daily maxima is very good. However, the agreement with actual trends in yearly one-hour maxima is fair to poor.

Table 12.9 Test of Azusa and Pomona Control Models for Yearly One-Hour Maximum NO_2

Station	Precursor Changes		Predicted Nine-Year Change in Yearly One-Hour Max. NO_2	Actual Nine-Year NO_2 Conc. Changes	
	NO_x	RHC		Yearly One-Hour Max.	99th Percentile of Daily Max.
Azusa	+40%	-10%	+34%	+39%	+35%
Pomona	+25%	-15%	+11%	+28%	+11%
Average	+33%	-13%	+23%	+34%	+23%

In a qualitative sense, the Azusa and Pomona models perform significantly poorer than the models for central and coastal Los Angeles. The Azusa and Pomona models predict that maximum NO_2 should have been reduced relative to annual mean NO_2 because of hydrocarbon control. This effect is not apparent in the historical air quality trends at Azusa and Pomona. There are several possible reasons for this discrepancy. First, statistical air quality fluctuations may be masking a real decline in maximal NO_2 relative to annual mean NO_2. Second, our estimates of RHC changes for Azusa and Pomona may be in error; it is possible that these high-growth sites have not experienced a decrease in hydrocarbons. Third, the neglect of transport, a potential error in all the models, may be a more significant error at Azusa and Pomona. Maximal NO_2 concentrations at Azusa and Pomona occur during the evening, and transport phenomena may be an essential part of the evening maxima. Fourth, the Azusa and Pomona nighttime models may contain an invalid assumption. The benefit of hydrocarbon control on the evening maximum occurs because oxidant concentrations are a significant factor to the evening NO_2 maximum. We have assumed, in all cases, that oxidant concentrations are proportional to the RHC/NO_x ratio. This assumption may be less appropriate for Azusa and Pomona than for the central and coastal sites. Oxidant at Azusa and Pomona would probably depend more on overall precursor levels than on the RHC/NO_x ratio.

12.4 DENVER

This section tests the empirical control model for the Denver CAMP site against historical air quality trends at that location. Unlike the Los Angeles cases, where the tests could be performed against nine-year trends, the data for Denver permit a check only against five-year trends.

12.4.1 Precursor Trends, 1967-1972

Estimates of precursor trends are required to test the empirical control model. Best estimates of precursor trends at Denver are derived below by examining both emission data and ambient data.

Emission Trends

Historical emission trends for Denver have apparently never been documented[6,7]. It is possible to derive a very rough estimate of emission trends by combining a 1974 emission inventory for Denver[8] with national emission trends[9,10] and with data on growth rates in Denver[11]. Table 12.10 summarizes these results.

Table 12.10 indicates that hydrocarbon emissions in the Denver region remained essentially unchanged from 1967 to 1974, while NO_x emissions increased 35%. Since we are interested in the period from 1967 to 1972, five years instead of seven, these emission changes should be multiplied by five-sevenths. Accordingly, for the period of interest, hydrocarbon emissions remained constant and NO_x emissions increased about 25%.

The emission changes derived above can only be regarded as very crude estimates. It has been implicitly assumed that control strategies, fuel switches, etc., in Denver have paralleled nationwide developments. It has also been assumed that source growth near the CAMP monitor has paralled growth throughout the Denver AQCR. The potential error in our estimates of emission changes affecting the Denver CAMP site may be as high as ± 10% or 20%.

Ambient NO_x Trends

Five-year trends in ambient NO_x are determined by examining the change in four-year averages of annual mean NO_x,[*] from 1965-1968 to 1970-1973. A longer averaging period is chosen for Denver than for Los Angeles because the Denver data are less complete and appear to contain more noise.

Annual mean NO_x at Denver changed from 6.95 pphm in 1965-1968 to 8.83 pphm in 1970-1973, an increase of 27%. This agrees almost exactly

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[*] Our estimates of annual mean NO_x are based on averages of quarterly means for NO and NO_2. In some cases, the SAROAD output did not list the quarterly mean concentration. When this was the case, we estimated mean NO (or NO_2) by taking an average of the 50th and 70th percentile concentrations.

Table 12.10 Estimates of Hydrocarbon and NO_x Emission Trends for the Denver Region

Source Category	1974 Emissions (Tons/Day)[8]	Nationwide Emission Change[a] 1974 ÷ 1967	Estimated Denver Emission Change[b] 1974 ÷ 1967	Estimated Emissions in 1967 (Tons/Day)
HYDROCARBONS				
Motor Vehicles	199	0.85	0.98	203
Aircraft	6	1.0	1.15	5
Gasoline Marketing	12	0.98	1.13	11
Other Stationary Sources	21	1.06	1.22	17
Total	238			236
NITROGEN OXIDES				
Motor Vehicles	88	1.24	1.43	62
Aircraft	4	1.1	1.27	3
Stationary Sources	108	1.13	1.30	83
Total	200			148

(a) Based on EPA documents[9,10]. Note that these two EPA documents do not agree in the common year, 1970. Our estimates for the change from 1967 to 1974 are based on relative changes from 1967 to 1970[9] and 1970 to 1974[10].

(b) Nationwide change has been factored by 1.15, the ratio of the seven-year population increase in the Denver Metropolitan Area (1.25) to the seven-year population increase nationwide (1.09), [11].

with the estimated five-year increase in NO_x emissions, 25%. Although the agreement is, no doubt, partly fortuitous, it does provide us with some confidence in air estimates of five-year NO_x trends at the Denver CAMP site.

Ambient NMHC Trends

Ambient hydrocarbon trend data at Denver are available only for total hydrocarbons. Using an empirical formula relating NMHC to THC at Denver,* the THC trends can be transformed into NMHC trends. We estimate that annual average NMHC in Denver changed from 72 pphm in 1965-1968 to 80 pphm in 1970-1973, an increase of 11%. This disagrees somewhat with the estimate that hydrocarbon emissions remained constant over the five-year period.

Best Estimates of Precursor Trends

Best estimates of precursor trends at Denver can be derived by considering both the emission trend data and the ambient trend data. In arriving at these estimates, greatest emphasis should be placed on the ambient data because of the crude nature of the emission calculations. Table 12.11 presents our best estimates of NO_x and NMHC trends from 1967 to 1972 along with approximate error bounds based on a subjective analysis of the uncertainties.

Table 12.11 Best Estimates of Five-Year NO_x and NMHC Trends at Denver

Station	NO_x Change 1967-1972	NMHC Change 1967-1972
Denver	+25% ± 5%	+5% ± 10%

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*Based on data for 1969-1973, this formula is NMHC =0.6[THC - 135 pphm].

12.4.2 Test of the Empirical Control Model

The empirical control model can be tested by entering the precursor trends in Table 12.11 into the control models for Denver (Tables 11.10a and 11.11a). The resulting predictions of NO_2 trends are then compared with actual five-year trends in ambient NO_2 concentrations.

Table 12.12 presents the test for annual mean NO_2. The actual increase in annual mean NO_2 concentrations (8%) is significantly less than the predicted increase (26%). This disagreement probably has little to do with hydrocarbon trends since hydrocabon changes were very small. The reason annual mean NO_2 trends did not follow NO_x trends is not obvious, but the discrepancy may be due to errors in the ambient data or undocumented changes in monitoring procedures for NO_2 or NO_x.

Table 12.12 Test of Denver Control Model for Annual Mean NO_2

Station	Precursor Changes 1967-1972		Predicted Five-Year Change in Annual Mean NO_2 Conc.	Actual Five-Year Change in Annual Mean NO_2 Conc.*
	NO_x	RHC		
Denver	+25%	+5%	+26%	+8%

Table 12.13 presents the test for yearly one-hour maximum NO_2. Again, the actual increase in ambient NO_2 are less than the increases predicted by the control model. This disagreement would appear to have little to do with the hydrocarbon effect since hydrocarbons changed very little over the five-year period.

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*Based on change in four-year averages from 1965-1968 to 1970-1973

Table 12.13 Tests of Denver Control Model for Yearly Maximum One-Hour NO_2

Station	Precursor Changes 1967-1972		Predicted Five-Year Change in Yearly One-Hour Max. NO_x	Actual Five-Year NO_2 Conc. Changes	
	NO_x	RHC		Yearly One-Hour Max.	99th Percentile of Daily Max.
Denver	+25%	+5%	+22%	+11%	+17%

Testing of the empirical control model for Denver against historical air quality trends has not been very fruitful. We cannot really test the hydrocarbon effect predicted by the models, since hydrocarbon changes have been relatively small over the five-year test period. The control models indicate that the historical decrease in the RHC/NO_x ratio should have produced a slight reduction in the ratio of maximal NO_2 concentrations to mean NO_2 concentrations. This effect is not apparent in the actual trends. However, the predicted effect is so small that we could not really expect to discern it in the ambient trends.

12.5 CHICAGO

In this section, the empirical control model for the Chicago CAMP site is checked against historical trends at that location. The verification study is conducted for an eight-year period, 1964 to 1972.

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*Based on changes in four-year averages from 1965-1968 to 1970-1973. Note that the original data for yearly maxima have been revised according to the results of our data quality check.

12.5.1 Precursor Trends, 1964-1972

Best estimates of historical precursor trends in Chicago are derived below by considering both emission data and ambient precursor data.

Emissions

Contacts with air pollution control agencies in Chicago[12,13] reveal that a study of historical emission trends has never been conducted for that region. Following the procedures used for Denver, crude estimates of historical emission trends can be derived for Chicago. These results are summarized in Table 12.14. Table 12.14 indicates that hydrocarbon emissions in Chicago remained nearly constant from 1964 to 1972, while NO_x emissions increased by 33%.

As was the case with Denver, the emission trend estimates for Chicago must be regarded as very approximate. The potential errors in the estimates of emission changes affecting the Chicago CAMP site may be as great as ± 10% to 20%.

Ambient NO_x Trends

Eight-year trends in ambient NO_x at Chicago are determined from the change in four-year averages of annual mean NO_x, from 1962-1965 to 1970-1973.* Annual mean NO_x at Chicago changed from 7.03 pphm in 1962-1965 to 9.93 pphm in 1970-1973, a net increase of 41%. This is in fair agreement with the estimated emission increase of 33%.

Ambient NMHC Trends

Ambient hydrocarbon trend data at Chicago are available only for total hydrocarbons. The THC trends can be transformed into NMHC trends

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*Data for 1971 have been omitted for NO_x and NO_2 because of problems with the Chicago NO_2 monitor during that year. The poor quality of NO_2 data during parts of 1971 is obvious from a scan of the hourly data.

Table 12.14 Estimates of Hydrocarbon and NO_x Emission Trends for Chicago

Source Category	1972 Emissions[a] (Tons/Day)	Nationwide Emission Change[c] 1972 ÷ 1964	Estimated Chicago Emission Change[d] 1972 ÷ 1964	Estimated Emissions in 1964 (Tons/Day)
HYDROCARBONS				
Motor Vehicles	192	0.95	0.93	206
Aircraft	12[b]	1.15	1.13	11
Gasoline Marketing	35	0.96	0.94	37
Other Stationary Sources	124	1.14	1.12	111
Total	363			365
NITROGEN OXIDES				
Motor Vehicles	132	1.29	1.26	105
Aircraft	8[b]	1.25	1.23	7
Stationary Sources	179	1.43	1.40	128
Total	319			240

(a) A 1973 inventory was obtained from reference [13]. We made some slight adjustments to make this inventory representative of 1972.

(b) The aircraft emission data available from reference [13] seemed highly dubious, especially in the ratio of hydrocarbon to NO_x emissions. We have adjusted the aircraft emissions somewhat, decreasing them for hydrocarbons and increasing them for NO_x. Since this is a minor source category, these adjustments are not of great consequence.

(c) Based on EPA documents[9,10]. Note that these two EPA documents do not agree in the common year, 1970. Our estimates for the change from 1964 to 1972 are based on relative changes from 1964 to 1970[9] and 1970 to 1972[10].

(d) Nationwide change has been factored by 0.98, the ratio of eight-year population increase in the Chicago region (1.08) to the eight-year population increase nationwide (1.10)[11].

using an empirical formula relating THC to NMHC.[*] In this way, we estimate that annual average NMHC concentrations at Chicago changed from 136 pphm in 1962-1965 to 90 pphm in 1970-1973. This decrease in ambient NMHC, 36%, differs greatly from our estimate that hydrocarbon emissions did not change from 1964 to 1972.

One possible reason for the discrepancy between estimated hydrocarbon emissions trends and ambient trends could be errors in the ambient data. As noted previously, ambient hydrocarbon data tend to be of poorer quality than other types of aerometric data[4].

A second reason for the discrepancy could be that the estimate of hydrocarbon emission trends in Chicago is overly conservative. Contacts with the City of Chicago Department of Environmental Control reveal that their control program did not start to focus on hydrocarbons until 1975. However, from 1964 to 1974 an exodus of some large emission sources from Chicago apparently did occur for economic reasons. This exodus of emission sources may have reduced hydrocarbon emissions in Chicago relative to our estimates based on population growth patterns and nationwide control strategies.

Best Estimates of Precursor Trends

Table 12.15 presents our best estimates of precursor trends in Chicago from 1964 to 1972. In arriving at these estimates, greatest emphasis has been placed on ambient trend data because of the crude nature of the emission calculations.

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[*] Based on data for 1969-1973, this formula is NMHC = .6[THC - 78 pphm].

Table 12.15 Best Estimates of Eight-Year NO_x and NMHC Trends at Chicago

Station	NO_x Change 1964-1972	NMHC Change 1964-1972
Chicago	+40% ± 10%	-25% ± 20%

12.5.2 Test of the Empirical Control Model

Table 12.16 presents the test of the empirical control model for annual mean NO_2 at Chicago. The predicted eight-year change in annual mean NO_2 is based on Table 11.12a, which indicates annual mean NO_2 should be directly proportional to NO_x control with no effect from hydrocarbon reductions. The agreement between predicted trends and actual trends for annual mean NO_2 is quite good.

Table 12.16 Test of the Chicago Control Model for Annual Mean NO_2

Station	Precursor Changes 1967-1972		Predicted Eight-Year Change in Annual Mean NO_2 Conc.	Actual Eight-Year Change in Annual Mean NO_2 Conc.*
	NO_x	RHC		
Chicago	+40%	-20%	+40%	+38%

Table 12.17 presents the test of the empirical control model for yearly maximum NO_2. The empirical control model (Table 11.13a) indicates that yearly maximum one-hour NO_2 should be directly proportional to NO_x control and independent of hydrocarbons. However, the historical

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[*] Based on change in four-year average from 1962-1965 to 1970-1973.

NO_2 trends indicate that maximal NO_2 concentrations have decreased relative to NO_x concentrations.

Table 12.17 Test of the Chicago Control Model for Yearly Maximum One-Hour NO_2

Station	Precursor Changes 1964-1972		Predicted Eight-Year Change in Yearly One-Hour Max. NO_2	Actual Eight-Year NO_2 Conc. Changes*	
	NO_x	RHC		Yearly One-Hour Max.	99th Percentile of Daily Max.
Chicago	+40%	-20%	+40%	+15%	+26%

The historical trends for annual mean NO_2 confirm the predictions of the empirical control models for Chicago, but the historical trends for maximal NO_2 do not. The historical trends for maximal NO_2 appear to be more consistent with the empirical control models for other cities, which indicated that hydrocarbon reductions would yield a benefit in terms of maximal NO_2 concentrations. It is possible that this hydrocarbon effect really does occur in Chicago during the summer daytime period (the season and time when the yearly maximum occurs), but that the statistical model for the summer daytime period in Chicago somehow failed to discern the effect. In this regard, it should be noted that the statistical model for the winter daytime period in Chicago did indicate a significant hydrocarbon effect.

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*Based on change in four-year average from 1962-1965 to 1970-1973. Note that the original data for yearly maxima have been revised according to the results of our data quality check.

12.6 SUMMARY OF VALIDATION STUDIES

Validation studies for the empirical NO_2 control models have been conducted for 5 areas: the central Los Angeles area, coastal Los Angeles area, inland Los Angeles area, Denver, and Chicago. In the central and coastal Los Angeles areas, the model predictions agreed quite well with historical NO_2 trends. The historical air quality trends in these 2 areas confirmed the conclusion that hydrocarbon reductions would have little impact on annual mean NO_2 concentrations but would bring moderate benefits in terms of maximal NO_2 concentrations.

The test for the inland Los Angeles area was less successful. The historical air quality trends did not confirm the model predictions that hydrocarbon control would reduce maximal NO_2 concentrations relative to mean NO_2 concentrations. Several reasons for the disagreement between predicted and actual trends at the inland Los Angeles sites have been discussed in Section 12.3.2. In particular, we noted that the neglect of transport and the assumed relationship of oxidant to the NMHC/NO_x ratio may be least appropriate for the inland Los Angeles sites.

Historical trends at Denver did not provide a proper test for the empirical control model. The existence of a hydrocarbon effect on NO_2 concentrations could not be checked with trend data because hydrocarbon levels remained essentially unchanged at Denver during the period of interest.

At Chicago, the empirical models indicated that hydrocarbons would affect neither annual mean nor yearly maximal NO_2 concentrations. The historical trends confirmed this conclusion for annual mean NO_2, but seemed to indicate that yearly maximum NO_2 had been reduced by hydrocarbon control.

In a general way, the studies of historical air quality trends do seem to confirm the qualitative conclusions of the empirical control models. Although the empirical control models vary with location, season, and time of day, three general conclusions are apparent:

1. With other factors held constant, annual mean and yearly maximum NO_2 concentrations are directly proportional to NO_x control.
2. Hydrocarbon control provides very slight, essentially negligible, benefits in terms of annual mean NO_2 concentrations.
3. Hydrocarbon control provides moderate (less than proportional) reductions in yearly maximal NO_2 concentrations.

In an aggregated sense, these conclusions are supported by historical trends at the 4 study locations that have experienced hydrocarbon reductions. Table 12.18 summarizes this agreement. It is evident that hydrocarbon control has generally been associated with little effect on annual mean NO_2 concentrations and with moderate benefits in terms of yearly maximal NO_2 concentrations.

Table 12.18 Summary of Historical Precursor Trends and Ambient NO_2 Trends for the 4 Study Areas Experiencing Significant Hydrocarbon Control

Location	Trend Period (Years)	Precursor Changes		Ambient NO_2 Changes	
		NO_x	RHC	Annual Mean	99th Percentile of Daily Maxima
CENTRAL LOS ANGELES AREA (DOLA, Burbank, Reseda)	9	+15%	-28%	+12%	+2%
COASTAL LOS ANGELES AREA (Lennox, Long Beach, West LA)	9	+3%	-27%	+10%	+3%
INLAND LOS ANGELES AREA (Azusa, Pomona)	9	+33%	-13%	+24%	+23%
CHICAGO CAMP SITE	8	+40%	-25%	+38%	+26%
AVERAGE OF 4 AREAS		+23%	-23%	+21%	+14%

12.7 REFERENCES

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3. California Air Resources Board, Air Analysis Section, "Ten-Year Summary of California Air Quality Data, 1963-1972" and Supplements for 1973-1975, January 1974.

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11. U. S. Department of Commerce, "Statistical Abstract of the United States, 1975," Bureau of the Census, 1975.

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13.0 COMPARISON OF EMPIRICAL MODELS AGAINST SMOG-CHAMBER RESULTS

Section 7.1 of this report reviewed smog-chamber results concerning the dependence of NO_2 on the photochemical precursors, NO_x and NMHC. The review indicated that the various experimental studies agreed with respect to the dependence of NO_2 on NO_x input; both annual mean and yearly maximum NO_2 concentrations should be approximately proportional to NO_x input. The various chamber studies disagreed somewhat concerning the dependence of NO_2 on hydrocarbon input. However, we were able to arrive at the following consensus based on the chamber studies: Fifty-percent hydrocarbon control should have little effect--a change of ±10 on mean NO_2 concentrations--but should yield moderate benefits--a reduction of 10% to 20%--in terms of maximal NO_2.

The purpose of this chapter is to check the empirical control models against the conclusions based on smog-chamber experiments. In order to provide an appropriate basis for the comparison, we will consider only the daytime empirical models. The durations of the various smog-chamber tests ranged from six to twelve hours; thus, the chamber experiments basically represent daytime conditions.

The empirical control models for all 8 cities concur with the smog-chamber results concerning the dependence of NO_2 on NO_x control. The empirical models indicate that, with other factors held constant, mean and maximum NO_2 concentrations are approximately proportional to NO_x input. The slight deviations from proportionality that sometimes occur in the empirical models are all in the direction of a less-than-proportional relationship. Some of the smog-chamber experiments indicate similar slight deviations away from proportionality (see Figures 7.1, 7.2, 7.3, and 7.7).*

A more crucial test of the empirical control models involves the hydrocarbon effect. Tables 13.1 and 13.2 summarize the hydrocarbon effect predicted by the winter/daytime and summer/daytime models, respectively. Table 13.1 indicates that, at the 6 non-Houston sites, the predictions for winter/daytime maximum NO_2 agree extremely well with the conclusions based on smog-chamber results. For a 50% hydrocarbon reduction, the predicted changes in winter/daytime maxima range from an 8% decrease to a 25% decrease and average a 15% decrease over the 6 non-Houston sites. These results compare very well with the 10% to 20% decrease in maximal NO_2 indicated by our review of smog-chamber studies.

The empirical models indicate that 50% hydrocarbon control should produce anywhere from a 19% decrease to an 8% increase in winter/daytime mean NO_2. The average of the predicted changes for the 6 non-Houston sites is an 8% decrease. These results are fairly consistent with the conclusion based on the smog-chamber studies, that a 50% reduction in hydrocarbons could change mean NO_2 by about ± 10%.

The empirical control models generally indicate smaller hydrocarbon effects in summer than in winter. For 50% hydrocarbon control, predicted effects on summer daytime maximal NO_2 range from no change to a 19% decrease. The average predicted reduction in the summer maximum is 10% for the 6 non-Houston sites. The empirical models indicate that 50%

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*The reason for these deviations is discussed in Chapter 14.

Table 13.1 Predicted Impact of a 50% Hydrocarbon Reduction on Daytime NO_2 in the Winter

Empirical Model	Effect on Winter/Daytime Maximum* NO_2	Effect on Winter/Daytime Mean NO_2
Downtown Los Angeles	-25%	-14%
Lennox	-10%	- 5%
Azusa	-15%	- 8%
Pomona	-20%	-19%
Denver	- 8%	+ 8%
Chicago	-14%	- 8%
Houston/Mae	0%	0%
Houston/Aldine	0%	0%

*Maximum one-hour NO_2 during the entire season

Table 13.2 Predicted Impact of a 50% Hydrocarbon Reduction on Daytime NO_2 in the Summer

Empirical Model	Effect on Summer/Daytime Maximum* NO_2	Effect on Summer/Daytime Mean NO_2
Downtown Los Angeles	-19%	- 6%
Lennox	-16%	- 4%
Azusa	0%	+ 1%
Pomona	-17%	- 9%
Denver	- 5%	- 7%
Chicago	0%	0%
Houston/Mae	0%	0%
Houston/Aldine	0%	0%

*Maximum one-hour NO_2 during the entire season hydrocarbon control would produce anywhere from a 1% increase to a 9% decrease in summer/daytime mean NO_2. The average predicted change over the 6 non-Houston sites is a 4% decrease. These summer results are also very consistent with the conclusions based on smog-chamber tests.

The reader may be concerned about the differences in the hydrocarbon effect predicted for different locations. One possibility is that the hydrocarbon effect is universal and that the differences between cities are a product of the errors, or limitations, in the empirical models. In this case, the aggregate conclusions, that a 50% hydrocarbon reduction would decrease maximal NO_2 by 10% to 20% and would yield very slight (if any) benefits in mean NO_2, is most useful. The other possibility is that the NO_2/hydrocarbon relationship varies with location, depending on climatology, the existing $NMHC/NO_x$ ratio, and other factors. That the hydrocarbon effect may depend on local conditions is supported by the variance in the observed NO_2/hydrocarbon relationship under different smog-chamber conditions. All considered, the variability in the hydrocarbon effect observed at the 8 locations is probably due to both factors, errors in the empirical models and dependence of the hydrocarbon effect on local conditions.

14.0 CONCLUSIONS OF THE EMPIRICAL MODELING STUDY

The objective for Part II of this project was to characterize the relationship between NO_2 and precursors by statistical analysis of air monitoring data. In line with this objective, we have formulated empirical control models for nitrogen dioxide, applied these models to 8 cities, and tested them against smog-chamber results and historical air quality trends. This chapter summarizes the main conclusions resulting from the investigation.

14.1 SUMMARY OF THE 8-CITY STUDY

The empirical control models for nitrogen dioxide are based on regression equations between NO_2 and precursors, and on certain simple physical assumptions. The control models for annual mean NO_2 involve synthesis of submodels for daytime average NO_2 and nighttime average NO_2, for both summer and winter. The control models for yearly one-hour maximal NO_2 are derived from submodels for peak NO_2 under the conditions (e.g., season and time of day) when the yearly maximum is likely to occur.

The formulations of empirical models for the 8 selected locations proceeded smoothly with the exception of nighttime models for the 2 Houston locations. Lack of nighttime models for Houston/Mae and Houston/Aldine precluded development of annual mean or yearly maximum control models for those 2 sites. Accordingly, this summary is restricted to the 6 other sites studied.

14.1.1 Dependence of NO_2 on NO_x

The empirical models for all 6 locations (as well as the daytime models for the 2 Houston sites) point to the basic conclusion that both annual mean NO_2 and yearly maximal NO_2 are essentially proportional to NO_x input. With other factors held constant, reducing NO_x by 50% should halve both mean and maximal NO_2 concentrations.

The slight deviations away from proportionality that sometimes occur in the empirical models are all in the direction of a less-than-proportional relationship. As noted in Chapter 13, similar slight deviations away from proportionality are often observed in smog-chamber simulations. The empirical models exhibit these deviations only when a significant hydrocarbon effect exists (e.g., as in most of the models for yearly maximum NO_2). The slight deviations from proportionality result because reducing NO_x has the side effect of raising the $NMHC/NO_x$ ratio; this increase in the ratio may produce an increase in NO_2 relative to NO_x.

The conclusion that, with other factors held constant, NO_2 concentrations are essentially proportional to NO_x input is supported by smog-chamber results and historical trends. This conclusion is also considered reasonable on basic physical and chemical grounds.

14.1.2 Dependence of NO_2 on Hydrocarbons

Table 14.1 summarizes the effect of hydrocarbon control on yearly one-hour maximum NO_2 and on annual mean NO_2. Although the results vary from site to site, the aggregate conclusion is that 50% hydrocarbon control should yield slight-to-moderate reductions (about 10% to15%) in yearly maximum NO_2 and essentially negligible benefits (about 0% to 5%) in annual mean NO_2. As shown in previous chapters, this general conclusion is supported quite well by smog-chamber results and historical air quality trends.

Table 14.1 Predicted Impact of a 50% Hydrocarbon Reduction on Annual Mean NO_2 and Yearly One-Hour Maximum NO_2

Empirical Model	Effect on Yearly One-Hour Maximum NO_2	Effect on Annual Mean NO_2	Effect on the Maximum/Mean Ratio for NO_2
Downtown Los Angeles	-25%*	-6%	-20%
Lennox	-10%*	-2%	-8%
Azusa	-6%**	-2%	-4%
Pomona	-19%**	-11%	-9%
Denver	-8%*	+5%	-12%
Chicago	0%***	0%	0%
Average for 6 Locations	-11.3%	-2.7%	-8.8%

*Maximum occurs in winter/daytime period.

**Maximum occurs in winter/nighttime period.

***Maximum occurs in summer/daytime period.

Table 14.1 seems to indicate that the model predictions for the maximum/mean NO_2 ratio are more consistent from city to city than are the predictions for the yearly maximum NO_2 or annual mean NO_2. Where hydrocarbon control yields relatively high (or low) benefits in terms of maximal NO_2, hydrocarbon control also yields relatively high (or low) benefits in terms of mean NO_2. As remarked in Chapter 7, the various smog-chamber studies agreed that hydrocarbon control should reduce the maximal/mean NO_2 ratio but disagreed as to how this decrease would be produced (i.e., decreasing the maximum with no change in the mean vs. increasing the mean with no change in the maximum). Thus, there appears to be consistency between the types of variations observed in different smog-chamber studies and the types of variations observed in empirical models for different cities.

The variations in the empirical models among cities can be due either to errors in the individual models or to real variations in the NO_2/precursor relationship from one location to the next. The differences in the NO_2/precursor relationship found in different smog-chamber studies indicate the latter cause is certainly a possibility. However, considering the potential errors in the empirical models, we are more sure of the general conclusions concerning the NO_2/precursor relationship than we are of the specific models for individual cities.

14.2 CONFIDENCE IN THE RESULTS

The empirical control models developed here are subject to several limitations: the omission of meteorological variables, the neglect of transport, and the assumption that precursor changes produced by variance in meteorology can be used to model the effect of control strageties. The potential importance of these limitations was stressed in Chapter 10, where analyses with weather variables indicated that the observed effect of hydrocarbons on NO_2 might be partially an artifact produced by unaccounted for meteorological factors. Because of the uncertainties in the simplified empirical models we have employed, we could not place great confidence in our understanding of the NO_2/precursor relationship if it were based solely on the empirical models.

We become much more confident of our understanding of the NO_2/precursor relationship when we consider the empirical models in conjunction with smog-chamber studies and historical trend analysis. All three approaches yield results that are consistent with the same general conclusions:

- With other factors held constant, yearly maximal and annual mean NO_2 concentrations are essentially proportional to NO_x input.
- Hydrocarbon control yields slight-to-moderate benefits in yearly maximal one-hour NO_2; reducing hydrocarbons by 50% should decrease yearly maximal NO_2 by about 10% to 20%.
- Hydrocarbon control yields very slight, essentially negligible, benefits in annual average NO_2.
- The exact form of the NO_2/precursor relationship may vary somewhat from one location to the next, depending on climatic conditions, reaction times, and the existing hydrocarbon/NO_x ratio.

Although empirical models, smog-chamber simulations, and historical trend studies all involve uncertainties, the overall agreement between the three types of analyses indicates that we do have a basic understanding of the dependence of ambient NO_2 concentrations on precursor control.

APPENDIX A

STATION-YEARS WITH 75% COMPLETE DATA ON SAROAD AS OF 3-6-76 (INCLUDES CORRECTIONS DISCOVERED IN DATA QUALITY CHECK)

STATION NUMBER		CITY	STATE	MONITOR METHOD	YEAR	NUMBER HOURS	10TH	30TH	50TH	70TH	90TH	95TH	99TH	MAX	ARITH MEAN	GEOM MEAN	GEOM STD DEV
							MICROGRAMS PER CUBIC METER										
3	600002	PHO	ARI	1	1973	7905	9	9	9	38	94	132	169	413	35.0	19.2	2.8
5	230001	ANA	CAL	1	1967	6749	9	38	56	94	169	207	320	508	80.0	56.1	2.5
5	230001	ANA	CAL	1	1968	7356	9	56	94	113	207	282	395	639	103.0	74.3	2.5
5	230001	ANA	CAL	1	1969	7985	38	56	75	113	169	207	320	658	96.0	74.9	2.2
5	230001	ANA	CAL	1	1970	7429	9	56	75	113	169	207	320	639	92.0	69.7	2.3
5	230001	ANA	CAL	1	1971	7875	38	56	75	113	188	244	414	1015	98.0	73.2	2.3
5	230001	ANA	CAL	1	1972	8004	38	56	75	94	150	207	320	620	86.0	65.2	2.3
5	230001	ANA	CAL	1	1973	7340	38	56	75	113	169	226	395	921	98.0	78.5	2.0
5	230001	ANA	CAL	1	1974	7993	38	56	94	113	188	263	395	696	106.0	83.1	2.1
5	500002	AZU	CAL	1	1965	7012	9	38	56	94	150	188	282	677	74.0	49.4	2.7
5	500002	AZU	CAL	1	1966	7736	9	38	75	113	169	207	301	583	86.0	58.8	2.7
5	500002	AZU	CAL	1	1967	7690	9	38	75	113	188	226	320	602	90.0	60.1	2.8
5	500002	AZU	CAL	1	1968	7622	9	9	56	113	188	244	414	639	85.0	46.8	3.3
5	500002	AZU	CAL	1	1969	7853	9	56	75	113	188	226	338	658	94.0	65.6	2.6
5	500002	AZU	CAL	1	1970	7311	9	56	94	150	226	282	414	808	117.0	81.4	2.7
5	500002	AZU	CAL	1	1971	7998	9	75	113	132	207	263	395	696	116.0	84.9	2.5
5	500002	AZU	CAL	1	1972	8081	38	75	94	132	207	263	414	827	115.0	86.1	2.4
5	500002	AZU	CAL	1	1973	8096	38	75	94	150	226	263	376	602	117.0	92.5	2.1
5	500002	AZU	CAL	1	1974	8269	38	75	113	150	207	263	395	846	119.0	96.4	2.0
5	520001	BAK	CAL	1	1968	7416	9	38	56	94	132	169	226	414	71.0	53.7	2.3
5	520001	BAK	CAL	1	1970	7732	38	56	75	113	150	188	226	414	91.0	76.4	1.8
5	520001	BAK	CAL	1	1967	6922	9	38	56	75	132	150	226	357	65.0	47.9	2.4
5	520001	BAK	CAL	1	1969	7219	38	56	75	113	150	188	226	451	89.0	75.8	1.9
5	520003	BAK	CAL	1	1972	7729	9	38	56	75	113	132	188	282	59.0	43.7	2.4
5	520003	BAK	CAL	1	1973	7618	19	38	38	56	94	132	169	244	55.0	45.1	1.9
5	520003	BAK	CAL	1	1974	7641	19	38	38	56	113	132	169	282	54.0	44.1	1.9
5	540001	BAR	CAL	1	1974	6988	9	38	56	94	150	188	244	846	75.0	52.8	2.5
5	900002	BUR	CAL	1	1963	7143	38	56	94	132	226	282	451	733	111.0	84.0	2.2
5	900002	BUR	CAL	1	1964	7367	38	56	94	132	207	244	357	564	106.0	83.0	2.2
5	900002	BUR	CAL	1	1965	7674	38	75	113	150	244	320	489	884	120.0	95.0	2.3
5	900002	BUR	CAL	1	1966	7736	38	75	113	150	244	320	470	792	130.0	90.6	2.3
5	900002	BUR	CAL	1	1967	7682	56	94	132	188	320	395	602	1093	187.0	131.3	2.1
5	900002	BUR	CAL	1	1968	7583	75	132	169	226	376	470	658	1015	201.0	164.2	2.0
5	900002	BUR	CAL	1	1969	7753	75	113	150	207	320	414	583	940	181.0	149.7	1.9
5	900002	BUR	CAL	1	1970	7683	75	113	150	207	320	395	564	902	172.0	141.0	2.0
5	900002	BUR	CAL	1	1971	7833	56	113	150	207	320	395	564	996	173.0	130.2	2.1
5	900002	BUR	CAL	1	1974	8280	56	75	113	150	244	301	414	658	134.0	111.8	1.9
5	1030001	CAM	CAL	1	1972	7291	9	38	56	75	113	150	226	414	62.0	42.7	2.6
5	1030001	CAM	CAL	1	1973	7778	19	38	38	56	94	113	150	338	51.0	41.7	2.0
5	1260001	CHI	CAL	1	1971	7835	9	9	9	38	75	94	113	188	31.0	21.0	2.8
5	1260001	CHI	CAL	1	1972	7841	9	9	38	38	75	75	113	207	33.0	23.2	2.4
5	1260001	CHI	CAL	1	1973	7852	19	19	19	38	75	75	113	188	35.0	29.8	1.7
5	1260001	CHI	CAL	1	1974	7826	19	19	19	38	75	94	132	188	36.0	30.0	1.8
5	1360001	CHI	CAL	1	1974	8157	19	38	56	75	132	150	244	696	64.0	47.6	2.3
5	1600001	CON	CAL	1	1974	7772	19	38	38	56	94	113	169	376	51.0	42.0	1.9
5	1740001	COS	CAL	1	1974	7970	9	19	38	75	132	169	282	564	57.0	36.8	2.6
5	2220001	ELC	CAL	1	1972	7570	9	38	56	75	113	150	226	451	59.0	41.3	2.5
5	2220001	ELC	CAL	1	1973	7864	9	19	38	56	94	132	188	357	52.0	39.2	2.2
5	2080002	EUR	CAL	1	1973	7295	19	19	38	38	56	56	75	188	32.0	28.1	1.7
5	2800002	FRE	CAL	1	1963	7082	9	9	38	38	75	75	113	188	35.0	25.1	2.3

STATION NUMBER	CITY	STATE	MONITOR METHOD	YEAR	NUMBER HOURS	10TH	30TH	50TH	70TH	90TH	95TH	99TH	MAX	ARITH MEAN	GEOM MEAN	GEOM STD DEV
						MICROGRAMS PER CUBIC METER										
5 2800002	FRE	CAL	1	1964	7061	9	9	38	38	75	113	150	320	39.0	26.3	2.5
5 2800002	FRE	CAL	1	1968	7446	9	38	38	56	94	132	188	320	52.0	38.4	2.3
5 2800002	FRE	CAL	1	1969	7197	9	38	56	75	113	132	188	301	58.0	45.4	2.2
5 2800003	FRE	CAL	1	1972	7955	9	38	56	56	94	94	150	244	48.0	36.7	2.3
5 2800003	FRE	CAL	1	1973	7898	19	38	56	56	94	113	150	282	55.0	48.0	1.7
5 2800003	FRE	CAL	1	1974	7898	19	38	38	56	94	113	169	583	50.0	43.1	1.8
5 3420001	INO	CAL	1	1972	8011	9	9	9	38	56	75	113	263	28.0	19.6	2.3
5 3420001	INO	CAL	1	1973	8420	9	19	19	38	75	75	113	188	36.0	28.4	2.0
5 3420001	INO	CAL	1	1974	8281	9	19	19	38	56	75	94	169	31.0	25.1	1.9
5 3440001	ING	CAL	1	1963	7216	56	75	94	150	263	338	583	1090	132.0	101.8	2.1
5 3440001	ING	CAL	1	1964	6927	56	75	94	150	226	301	432	752	125.0	100.6	2.0
5 3620001	LAN	CAL	1	1970	8080	9	9	38	56	113	132	207	414	52.0	33.5	2.7
5 3620001	LAN	CAL	1	1971	7565	38	56	94	113	188	226	376	639	100.0	77.7	2.2
5 3620001	LAN	CAL	1	1972	7929	38	56	94	113	169	226	357	808	101.0	79.8	2.1
5 3620001	LAN	CAL	1	1973	7932	38	56	94	132	188	244	395	959	108.0	86.7	2.0
5 3620001	LAN	CAL	1	1974	7827	38	56	94	132	188	244	357	602	106.0	84.8	2.0
5 3740001	LAN	CAL	1	1972	8260	9	9	9	9	56	75	113	188	23.0	15.5	2.2
5 3740001	LAN	CAL	1	1973	8013	19	19	19	19	38	56	75	150	26.0	23.1	1.5
5 3740001	LAN	CAL	1	1974	8238	19	19	19	38	56	75	113	188	30.0	25.9	1.6
5 3900001	LEN	CAL	1	1966	7397	38	56	94	132	226	282	414	752	111.0	83.7	2.3
5 3900001	LEN	CAL	1	1967	7521	38	75	113	150	282	395	733	1260	147.0	108.3	2.4
5 3900001	LEN	CAL	1	1968	7351	38	75	113	150	263	338	508	1072	134.0	97.9	2.4
5 3900001	LEN	CAL	1	1969	7676	56	75	113	132	226	282	395	752	122.0	100.8	2.0
5 3900001	LEN	CAL	1	1970	8065	56	75	113	150	226	301	451	752	132.0	107.5	2.0
5 3900001	LEN	CAL	1	1971	8030	56	75	113	150	226	301	489	808	130.0	106.5	1.9
5 3900001	LEN	CAL	1	1972	8338	38	75	94	132	207	263	414	733	120.0	98.2	2.0
5 3900001	LEN	CAL	1	1973	8294	56	75	113	132	207	244	395	733	120.0	102.7	1.8
5 3900001	LEN	CAL	1	1974	8254	56	75	94	132	207	263	376	808	119.0	100.3	1.8
5 4020002	LIV	CAL	1	1972	8021	38	56	56	75	113	132	169	301	60.0	57.8	1.9
5 4020002	LIV	CAL	1	1973	8058	19	38	56	75	113	132	188	320	65.0	56.6	1.7
5 4020002	LIV	CAL	1	1974	8154	19	38	56	56	94	113	169	338	55.0	47.7	1.8
5 4100002	LON	CAL	1	1963	7140	38	56	94	132	263	320	489	1072	117.0	82.1	2.5
5 4100002	LON	CAL	1	1964	7081	38	56	94	132	226	282	414	1109	112.0	85.2	2.2
5 4100002	LON	CAL	1	1965	7814	38	56	75	113	207	263	451	865	104.0	75.6	2.3
5 4100002	LON	CAL	1	1966	7306	38	75	94	132	226	282	395	790	118.0	94.1	2.0
5 4100002	LON	CAL	1	1967	7505	56	75	113	150	263	338	489	865	141.0	112.2	2.0
5 4100002	LON	CAL	1	1968	7492	56	94	113	169	301	395	620	1316	156.0	118.5	2.2
5 4100002	LON	CAL	1	1969	7827	56	94	113	150	263	338	508	996	141.0	112.9	2.0
5 4100002	LON	CAL	1	1970	8073	56	94	132	169	263	338	508	978	148.0	121.9	2.0
5 4100002	LON	CAL	1	1971	8075	56	75	94	132	226	301	489	865	126.0	102.7	1.9
5 4100002	LON	CAL	1	1974	7890	56	75	113	150	226	263	395	696	126.0	107.2	1.8
5 4120001	LOS	CAL	1	1972	6769	9	56	75	113	169	226	357	639	88.0	62.9	2.5
5 4160001	LOS	CAL	1	1963	7044	38	56	94	132	244	320	489	1034	121.0	86.7	2.5
5 4160001	LOS	CAL	1	1964	7120	9	56	75	113	207	263	432	1316	106.0	74.6	2.5
5 4160001	LOS	CAL	1	1965	7616	38	75	113	150	263	338	508	1316	134.0	101.3	2.2
5 4160001	LOS	CAL	1	1966	7817	56	94	113	169	263	338	489	1504	146.0	119.2	2.0
5 4160001	LOS	CAL	1	1967	7781	38	75	94	132	226	320	508	1015	126.0	95.7	2.2
5 4160001	LOS	CAL	1	1968	7623	38	75	113	150	244	301	489	884	131.0	101.6	2.3
5 4160001	LOS	CAL	1	1969	7399	38	75	113	150	207	263	414	1504	121.0	95.4	2.2
5 4160001	LOS	CAL	1	1970	7902	38	75	113	150	263	338	508	1335	140.0	106.3	2.3

STATION NUMBER	CITY	STATE	MONITOR METHOD	YEAR	NUMBER HOURS	10TH	30TH	50TH	70TH	90TH	95TH	99TH	MAX	ARITH MEAN	GEOM MEAN	GEOM STD DEV
						MICROGRAMS PER CUBIC METER										
5 4180001	LOS	CAL	1	1971	8017	75	113	150	188	301	395	602	1391	173.0	144.1	1.9
5 4180001	LOS	CAL	1	1972	8215	56	94	132	169	244	320	489	733	145.0	120.5	1.9
5 4180001	LOS	CAL	1	1973	7717	56	75	113	150	207	263	395	1090	125.0	106.2	1.8
5 4180001	LOS	CAL	1	1974	7959	56	94	113	169	244	320	489	1203	142.0	117.1	1.9
5 4180002	LOS	CAL	1	1963	7364	9	38	56	94	188	244	414	771	88.0	59.9	2.6
5 4180002	LOS	CAL	1	1964	7376	38	56	75	113	188	226	376	752	93.0	68.7	2.3
5 4180002	LOS	CAL	1	1965	7282	38	56	94	132	244	320	508	996	121.0	88.8	2.3
5 4180002	LOS	CAL	1	1966	7779	38	56	94	132	207	263	432	884	109.0	83.2	2.2
5 4180002	LOS	CAL	1	1967	7632	38	56	94	132	226	301	432	940	114.0	89.3	2.1
5 4180002	LOS	CAL	1	1968	7798	56	75	113	150	244	320	508	884	136.0	110.4	2.0
5 4180002	LOS	CAL	1	1969	8103	56	75	94	132	207	263	395	902	119.0	99.0	1.9
5 4180002	LOS	CAL	1	1970	8008	56	75	113	132	226	301	451	978	126.0	103.2	2.0
5 4180002	LOS	CAL	1	1971	7918	56	94	113	150	244	320	508	1128	141.0	113.9	2.0
5 4180002	LOS	CAL	1	1972	8042	38	75	94	132	226	282	432	790	118.0	92.7	2.1
5 4180002	LOS	CAL	1	1973	8207	56	94	113	150	226	282	432	884	132.0	110.8	1.8
5 4180002	LOS	CAL	1	1974	8184	56	75	113	150	244	301	451	1029	134.0	112.6	1.8
5 4180017	LOS	CAL	1	1963	7139	38	75	94	132	244	320	508	940	123.0	92.8	2.2
5 4180017	LOS	CAL	1	1964	7199	56	75	113	132	226	263	432	827	124.0	101.3	2.0
5 4180017	LOS	CAL	1	1965	7400	56	75	113	150	244	320	489	1072	136.0	[illegible]	2.0
5 4180017	LOS	CAL	1	1966	7539	38	56	94	132	207	282	432	902	112.0	[illegible]	2.2
5 4180017	LOS	CAL	1	1967	7119	38	75	113	150	263	338	526	902	133.0	[illegible]	2.4
5 4200001	LOS	CAL	1	1966	7729	9	56	75	113	188	226	357	658	96.0	70.7	2.5
5 4200001	LOS	CAL	1	1967	7565	9	56	94	132	226	282	470	827	111.0	73.9	2.8
5 4200001	LOS	CAL	1	1968	7550	38	56	94	132	226	282	432	865	117.0	83.6	2.5
5 4200001	LOS	CAL	1	1969	7683	9	56	94	132	207	263	357	650	109.0	77.9	2.5
5 4200001	LOS	CAL	1	1970	7764	38	75	113	150	263	320	451	735	129.0	90.3	2.6
5 4200001	LOS	CAL	1	1971	7881	38	75	113	169	244	301	432	714	132.0	98.9	2.4
5 4200001	LOS	CAL	1	1972	8318	38	75	113	150	244	301	451	790	129.0	96.1	2.4
5 4200001	LOS	CAL	1	1973	8506	38	75	113	132	207	263	376	696	118.0	96.5	2.0
5 4200001	LOS	CAL	1	1974	8390	38	75	94	132	207	244	376	664	109.0	88.8	2.0
5 4200022	LOS	CAL	1	1964	6910	56	94	113	169	244	301	432	1128	143.0	120.0	1.9
5 4200022	LOS	CAL	1	1965	6980	56	75	113	150	263	338	489	1128	142.0	115.9	1.9
5 4200022	LOS	CAL	1	1966	7549	56	94	132	169	263	320	470	902	140.0	124.9	1.8
5 4260001	LYN	CAL	1	1974	7918	38	75	94	113	169	226	338	696	103.0	85.7	1.9
5 4720001	MOD	CAL	1	1972	7692	9	38	38	56	75	94	113	207	47.0	39.7	1.9
5 4720001	MOD	CAL	1	1973	7866	19	38	38	56	75	94	150	244	52.0	46.4	1.8
5 4720001	MOD	CAL	1	1974	8101	19	38	56	56	94	113	150	338	53.0	46.6	1.7
5 4840001	MON	CAL	1	1969	7691	9	9	38	38	75	94	132	207	37.0	25.0	2.4
5 4840001	MON	CAL	1	1972	8271	9	9	9	38	56	75	94	207	26.0	18.2	2.2
5 4840001	MON	CAL	1	1973	8006	19	19	19	38	56	75	94	226	32.0	27.8	1.6
5 4840001	MON	CAL	1	1974	8069	19	19	19	19	38	56	94	169	26.0	23.6	1.5
5 5000005	NAP	CAL	1	1974	8281	19	38	38	56	75	94	132	263	49.0	43.1	1.7
5 5120001	NEW	CAL	1	1972	8115	9	38	56	94	150	169	282	583	70.0	55.7	2.4
5 5120001	NEW	CAL	1	1973	8180	19	38	56	75	132	150	207	376	71.0	59.0	1.9
5 5120001	NEW	CAL	1	1974	8174	19	38	56	75	94	113	150	320	57.0	48.9	1.8
5 5150001	NOR	CAL	1	1974	8146	19	38	38	56	94	132	207	414	53.0	41.9	2.0
5 5300003	OAK	CAL	1	1965	7444	9	38	56	75	113	150	226	432	58.0	42.7	2.4
5 5300003	OAK	CAL	1	1967	8080	9	38	56	75	150	188	282	620	73.0	53.9	2.3
5 5300003	OAK	CAL	1	1968	8112	9	38	56	75	113	150	226	470	64.0	47.2	2.4
5 5300004	OAK	CAL	1	1969	7412	9	38	56	75	113	169	263	470	62.0	44.1	2.5

STATION NUMBER	CITY	STATE	MONITOR METHOD	YEAR	NUMBER HOURS	10TH	30TH	50TH	70TH	90TH	95TH	99TH	MAX	ARITH MEAN	GEOM MEAN	GEOM STD DEV
						MICROGRAMS PER CUBIC METER										
5 5300004	OAK	CAL	1	1970	7184	9	38	75	94	132	169	263	508	75.0	58.0	2.2
5 5300004	OAK	CAL	1	1971	7388	38	38	75	75	132	169	244	470	75.0	60.2	2.0
5 5300004	OAK	CAL	1	1972	7942	9	38	56	75	113	150	226	376	67.0	53.8	2.1
5 5300004	OAK	CAL	1	1973	8170	38	38	56	75	113	150	226	414	70.0	59.0	1.8
5 5300004	OAK	CAL	1	1974	7974	19	38	56	75	113	132	207	470	60.0	49.5	1.9
5 5340001	OJA	CAL	1	1972	7188	9	9	9	38	75	75	113	357	28.0	19.1	2.3
5 5640001	PAL	CAL	1	1972	8220	9	9	9	38	56	75	94	188	26.0	17.7	2.3
5 5640001	PAL	CAL	1	1973	7062	19	19	19	38	56	75	94	169	32.0	26.2	1.9
5 5640001	PAL	CAL	1	1974	8450	9	19	19	19	56	56	75	132	24.0	21.0	1.7
5 5760001	PAS	CAL	1	1963	6957	9	56	75	113	188	226	357	620	93.0	67.3	2.4
5 5760001	PAS	CAL	1	1964	7432	38	75	94	132	207	244	357	677	109.0	86.7	2.1
5 5760001	PAS	CAL	1	1965	7417	38	56	94	113	207	244	376	639	105.0	81.1	2.2
5 5760001	PAS	CAL	1	1966	7563	38	75	94	132	188	244	376	620	106.0	81.4	2.3
5 5760001	PAS	CAL	1	1967	7711	56	75	94	132	207	263	414	696	121.0	99.4	2.0
5 5760001	PAS	CAL	1	1974	8085	56	94	113	150	226	282	432	884	130.0	117.8	1.8
5 5880001	PIT	CAL	1	1969	7890	9	9	38	56	75	94	132	188	39.0	27.8	2.4
5 5880001	PIT	CAL	1	1970	7611	9	9	38	56	75	94	132	263	43.0	31.4	2.4
5 5880001	PIT	CAL	1	1971	7733	9	9	38	56	75	94	132	282	39.0	28.2	2.4
5 5880001	PIT	CAL	1	1972	7639	9	9	9	38	56	56	94	132	26.0	18.6	2.2
5 5880001	PIT	CAL	1	1973	7814	19	19	38	38	75	94	132	226	40.0	34.2	1.7
5 5880001	PIT	CAL	1	1974	7895	19	19	38	56	75	75	113	207	39.0	32.2	1.9
5 6040001	POM	CAL	1	1966	7634	56	75	113	150	207	244	338	583	118.0	97.5	2.0
5 6040001	POM	CAL	1	1967	7605	56	94	113	150	226	263	395	696	131.0	111.4	1.8
5 6040001	POM	CAL	1	1968	7848	75	94	132	169	244	301	470	790	140.0	126.0	1.8
5 6040001	POM	CAL	1	1969	7936	56	94	132	169	244	301	414	808	145.0	128.1	1.8
5 6040001	POM	CAL	1	1970	7930	75	113	150	188	263	320	451	846	158.0	135.4	1.8
5 6040001	POM	CAL	1	1971	8120	75	94	132	169	244	301	451	752	146.0	125.4	1.8
5 6040001	POM	CAL	1	1974	8270	56	94	113	150	207	263	357	658	129.0	114.2	1.7
5 6160002	RED	CAL	1	1972	7819	9	9	38	38	56	75	113	169	34.0	25.6	2.2
5 6160002	RED	CAL	1	1973	7896	19	19	38	38	56	75	113	169	35.0	30.0	1.7
5 6160002	RED	CAL	1	1974	7735	19	19	38	38	56	75	113	207	34.0	29.0	1.7
5 6250001	RED	CAL	1	1971	7463	9	38	75	94	150	188	263	602	79.0	58.7	2.4
5 6250001	RED	CAL	1	1972	7420	9	38	56	94	150	188	244	432	74.0	53.5	2.5
5 6250001	RED	CAL	1	1973	6063	38	56	75	94	150	169	226	357	82.0	70.2	1.8
5 6250001	RED	CAL	1	1974	7734	19	38	56	94	132	150	226	564	72.0	59.2	1.9
5 6240001	RED	CAL	1	1968	7461	9	38	38	56	94	132	207	395	50.0	38.8	2.5
5 6240001	RED	CAL	1	1969	7717	9	38	56	75	132	169	282	526	62.0	43.1	2.5
5 6240001	RED	CAL	1	1970	8003	9	38	56	75	113	150	226	489	64.0	49.1	2.3
5 6240001	RED	CAL	1	1971	7901	9	38	56	56	94	132	207	395	54.0	41.2	2.3
5 6240001	RED	CAL	1	1972	7795	9	38	56	75	94	113	169	263	56.0	45.0	2.1
5 6240001	RED	CAL	1	1973	7962	19	19	38	56	75	113	169	301	46.0	38.2	1.8
5 6240001	RED	CAL	1	1974	8166	9	19	38	56	113	132	244	620	51.0	35.0	2.4
5 6330001	RIC	CAL	1	1967	7407	9	38	56	75	113	132	188	395	62.0	45.9	2.4
5 6330001	RIC	CAL	1	1968	7504	9	38	56	94	132	150	188	376	70.0	53.0	2.4
5 6330001	RIC	CAL	1	1971	8237	9	9	38	56	75	94	132	357	36.0	25.2	2.0
5 6330002	RIC	CAL	1	1969	7097	9	38	56	75	132	150	226	545	63.0	45.5	2.5
5 6330003	RIC	CAL	1	1974	8038	19	38	56	56	94	113	150	263	52.0	44.2	1.8
5 6400001	RIV	CAL	1	1966	6880	9	38	56	94	150	188	282	470	70.0	45.2	2.0
5 6400001	RIV	CAL	1	1967	6738	9	38	75	94	169	207	282	583	82.0	55.0	2.7
5 6400005	RIV	CAL	1	1974	7744	38	56	75	113	169	188	263	470	94.0	80.5	1.8

STATION NUMBER	CITY	STATE	MONITOR METHOD	YEAR	NUMBER HOURS	10TH	30TH	50TH	70TH	90TH	95TH	99TH	MAX	ARITH MEAN	GEOM MEAN	GEOM STD DEV
						MICROGRAMS PER CUBIC METER										
5 0555001	[illegible]	CAL	1	1974	8232	9	19	38	56	94	132	188	376	50.0	36.2	2.3
5 0580002	SAC	CAL	1	1963	7487	9	38	56	75	150	188	263	545	68.0	45.2	2.7
5 0580002	SAC	CAL	1	1964	7173	38	38	75	94	150	188	282	602	77.0	61.5	2.1
5 0580002	SAC	CAL	1	1965	7600	38	56	56	75	113	150	263	564	73.0	59.8	2.0
5 0580002	SAC	CAL	1	1966	7336	9	38	38	56	94	113	207	508	50.0	36.1	2.4
5 0580002	SAC	CAL	1	1967	6930	9	38	56	75	113	150	244	564	66.0	51.1	2.2
5 0580002	SAC	CAL	1	1969	8116	9	38	56	75	94	132	188	376	55.0	40.9	2.3
5 0580002	SAC	CAL	1	1970	7925	9	38	38	56	94	113	169	282	53.0	41.4	2.2
5 0580002	SAC	CAL	1	1971	7524	9	38	38	56	75	113	150	470	46.0	35.4	2.2
5 0580003	SAC	CAL	1	1972	7817	9	38	38	56	75	113	150	263	49.0	39.2	2.1
5 0580003	SAC	CAL	1	1973	7912	19	38	38	56	94	113	188	414	54.0	46.5	1.7
5 0580003	SAC	CAL	1	1974	7724	19	38	38	56	94	113	169	320	52.0	43.6	1.8
5 0620001	SAL	CAL	1	1967	7751	9	9	9	38	56	75	94	188	27.0	19.0	2.2
5 0620001	SAL	CAL	1	1968	8117	9	9	38	38	75	75	113	188	32.0	22.1	2.4
5 0620001	SAL	CAL	1	1969	8143	9	9	38	56	75	94	113	244	41.0	30.2	2.3
5 0620001	SAL	CAL	1	1970	8114	9	9	38	56	75	94	113	188	41.0	31.0	2.3
5 0620001	SAL	CAL	1	1971	6887	9	9	38	56	75	94	113	207	42.0	30.0	2.4
5 0620001	SAL	CAL	1	1972	8135	9	9	38	56	75	94	113	207	42.0	31.0	2.3
5 0620001	SAL	CAL	1	1973	8411	19	19	38	56	75	94	113	263	43.0	36.5	1.8
5 0620001	SAL	CAL	1	1974	8159	19	19	38	38	75	94	113	282	39.0	32.9	1.8
5 0660001	SAN	CAL	1	1971	6575	38	56	75	113	169	226	320	508	93.0	71.2	2.3
5 0660001	SAN	CAL	1	1972	6891	38	56	75	94	150	188	263	545	85.0	66.8	2.2
5 0660001	SAN	CAL	1	1973	7480	19	38	75	94	132	169	226	357	76.0	61.0	2.0
5 0660001	SAN	CAL	1	1974	8058	19	38	75	94	150	188	263	846	83.0	62.2	2.3
5 0680001	SAN	CAL	1	1963	7573	9	9	38	56	113	150	244	620	51.0	31.5	2.8
5 0680001	SAN	CAL	1	1964	7120	9	9	9	38	94	132	207	658	35.0	19.5	2.7
5 0680001	SAN	CAL	1	1965	6867	9	9	9	38	94	132	226	978	41.0	23.5	2.8
5 0680001	SAN	CAL	1	1966	6639	9	9	38	94	132	169	282	752	61.0	34.8	3.1
5 0680001	SAN	CAL	1	1967	7189	9	9	9	38	75	94	188	639	32.0	19.3	2.5
5 0680004	SAN	CAL	1	1974	7895	19	19	38	56	113	132	188	470	50.0	37.5	2.2
5 0820003	SAN	CAL	1	1965	6714	9	9	9	9	56	75	132	320	21.0	14.0	2.2
5 0820005	SAN	CAL	1	1967	7333	9	9	38	56	94	113	188	395	42.0	28.6	2.5
5 0820005	SAN	CAL	1	1968	7550	9	38	56	75	113	150	244	639	65.0	47.3	2.4
5 0820005	SAN	CAL	1	1970	7287	9	9	38	56	94	113	169	338	45.0	30.0	2.6
5 0820005	SAN	CAL	1	1971	7406	9	38	56	94	150	188	320	752	74.0	48.4	2.7
5 0860002	SAN	CAL	3	1963	6691	38	56	75	113	150	188	320	620	92.0	74.7	2.0
5 0860002	SAN	CAL	3	1964	6836	38	75	94	113	169	226	395	771	106.0	86.0	2.0
5 0860003	SAN	CAL	1	1969	8140	38	56	75	94	132	169	263	639	80.0	66.8	1.9
5 0860003	SAN	CAL	1	1972	7518	38	56	56	75	94	113	188	620	64.0	55.0	1.8
5 0860003	SAN	CAL	1	1973	7789	38	38	56	75	94	132	207	395	64.0	56.2	1.6
5 0860003	SAN	CAL	1	1974	7751	19	38	56	75	94	113	150	301	56.0	49.1	1.7
5 0880001	SAN	CAL	1	1963	6680	38	56	75	94	150	169	301	602	86.0	68.1	2.1
5 0880001	SAN	CAL	1	1964	6856	38	56	94	113	169	226	376	771	99.0	77.8	2.2
5 0880002	SAN	CAL	1	1966	7543	9	38	56	56	94	132	207	451	56.0	41.4	2.3
5 0880002	SAN	CAL	1	1967	8012	9	38	56	75	113	150	244	658	63.0	47.0	2.3
5 0880002	SAN	CAL	1	1969	7853	9	38	56	75	132	169	244	395	67.0	51.2	2.2
5 0980003	SAN	CAL	1	1966	6738	38	56	75	94	150	188	320	508	81.0	64.9	2.1
5 0980003	SAN	CAL	1	1967	7892	9	56	56	94	150	207	301	508	80.0	59.6	2.3
5 0980003	SAN	CAL	1	1968	7829	38	38	56	75	132	169	282	545	71.0	55.9	2.1
5 0980004	SAN	CAL	2	1974	7614	19	38	56	75	113	150	263	545	67.0	53.7	2.0

STATION NUMBER	CITY	STATE	MONITOR METHOD	YEAR	NUMBER HOURS	10TH	30TH	50TH	70TH	90TH	95TH	99TH	MAX	ARITH MEAN	GEOM MEAN	GEOM STD DEV
						MICROGRAMS PER CUBIC METER										
5 6980004	SAN	CAL	1	1974	7791	38	56	56	75	132	169	282	564	76.0	63.2	1.8
5 7040001	SAN	CAL	1	1972	7597	9	9	38	38	75	94	113	226	37.0	27.2	2.3
5 7040001	SAN	CAL	1	1973	7817	19	19	38	38	75	75	113	207	41.0	35.3	1.7
5 7040001	SAN	CAL	1	1974	7813	19	19	38	38	75	75	113	169	38.0	32.7	1.7
5 7160001	SAN	CAL	1	1968	7893	9	38	56	75	113	132	226	451	62.0	48.2	2.2
5 7160001	SAN	CAL	1	1969	7714	9	38	56	75	94	113	169	338	55.0	40.9	2.3
5 7160001	SAN	CAL	1	1970	7560	9	38	56	56	94	113	150	320	53.0	42.0	2.1
5 7160001	SAN	CAL	1	1971	7999	9	38	38	56	75	94	113	226	42.0	32.9	2.2
5 7160001	SAN	CAL	1	1972	8248	9	38	38	56	75	94	132	263	46.0	36.7	2.1
5 7160001	SAN	CAL	1	1973	7846	19	38	56	75	94	113	169	357	58.0	50.2	1.8
5 7160001	SAN	CAL	1	1974	8290	19	38	56	56	94	94	132	320	55.0	49.1	1.6
5 7180002	SAN	CAL	1	1971	7586	9	9	38	56	132	169	282	658	54.0	30.9	3.0
5 7200001	SAN	CAL	1	1964	7105	9	9	38	56	75	94	132	338	38.0	27.8	2.3
5 7200001	SAN	CAL	1	1965	7385	9	38	56	56	94	113	169	583	53.0	40.7	2.2
5 7200002	SAN	CAL	1	1972	7744	38	56	56	75	113	132	169	301	67.0	56.2	2.0
5 7200004	SAN	CAL	1	1972	6922	38	38	56	75	94	113	150	395	59.0	52.4	1.7
5 7200004	SAN	CAL	1	1973	7656	19	38	56	75	94	113	150	282	57.0	49.7	1.7
5 7200004	SAN	CAL	1	1974	7861	19	38	56	75	94	113	169	451	58.0	49.2	1.8
5 7300001	SAN	CAL	1	1967	7855	9	9	9	38	56	75	113	169	28.0	19.9	2.3
5 7300001	SAN	CAL	1	1968	8182	9	9	9	38	56	75	113	226	27.0	19.2	2.3
5 7300001	SAN	CAL	1	1969	7950	9	9	9	38	56	75	113	282	26.0	17.6	2.3
5 7300001	SAN	CAL	1	1970	7799	9	9	9	9	38	56	75	113	20.0	14.8	2.0
5 7300001	SAN	CAL	1	1971	8040	9	9	9	38	56	56	75	169	23.0	17.3	2.1
5 7300001	SAN	CAL	1	1972	8065	9	9	38	38	56	75	113	263	32.0	23.5	2.3
5 7300001	SAN	CAL	1	1973	8103	19	19	19	38	38	56	75	169	27.0	24.2	1.5
5 7300001	SAN	CAL	1	1974	7963	19	19	19	19	38	56	75	150	25.0	22.8	1.4
5 7400001	SAN	CAL	1	1970	7762	9	9	38	38	56	75	113	263	34.0	26.2	2.2
5 7400002	SAN	CAL	1	1974	7936	19	19	38	38	75	75	113	282	37.0	31.0	1.8
5 6040002	STU	CAL	1	1965	7113	9	9	38	38	75	75	132	263	35.0	24.8	2.4
5 6040002	STU	CAL	1	1966	7496	9	9	38	38	75	94	132	301	34.0	23.2	2.4
5 6040002	STU	CAL	1	1967	7022	9	9	38	38	75	94	150	338	34.0	26.6	2.4
5 6040002	STU	CAL	1	1968	6908	9	38	56	75	113	150	188	414	58.0	42.0	2.5
5 6040002	STU	CAL	1	1969	6963	9	38	56	75	169	207	282	414	71.0	44.6	2.8
5 6040002	STU	CAL	1	1970	7508	9	9	38	38	75	75	132	320	36.0	26.1	2.3
5 6040002	STU	CAL	1	1971	7160	9	38	38	56	75	94	132	282	41.0	31.4	2.2
5 6040002	STU	CAL	1	1972	7029	9	38	38	56	75	94	113	207	43.0	34.2	2.2
5 6040002	STU	CAL	1	1973	7454	19	38	38	56	75	94	150	301	50.0	43.5	1.7
5 6040002	STO	CAL	1	1974	7570	38	38	56	75	94	113	169	357	60.0	53.7	1.6
5 6080001	SUN	CAL	1	1974	7819	19	56	75	94	132	169	282	583	77.0	63.3	1.9
5 6440003	UPL	CAL	1	1974	7184	38	75	94	132	207	244	320	714	112.0	87.6	2.2
5 6440004	UPL	CAL	1	1974	7754	38	56	75	113	169	188	263	526	92.0	77.6	1.9
5 6480003	VAL	CAL	1	1974	8048	19	38	38	56	75	94	132	263	49.0	43.4	1.7
5 6510001	VIC	CAL	1	1974	6597	19	38	56	94	150	169	282	414	70.0	50.7	2.4
5 6520001	VIS	CAL	1	1971	7606	9	38	38	56	94	113	169	282	45.0	33.1	2.3
5 6520001	VIS	CAL	1	1972	7936	9	9	38	56	75	94	132	226	40.0	28.9	2.4
5 6520001	VIS	CAL	1	1973	7832	19	19	38	56	75	94	132	226	45.0	38.6	1.8
5 6520001	VIS	CAL	1	1974	7804	19	19	38	56	75	94	132	244	43.0	36.5	1.8
5 6720001	WHI	CAL	1	1972	8303	56	94	113	150	244	320	470	1166	140.0	115.5	1.9
5 6720001	WHI	CAL	1	1973	8064	56	75	113	132	207	263	395	902	123.0	105.8	1.7
5 6720001	WHI	CAL	1	1974	8096	38	56	94	113	188	244	376	752	102.0	83.4	1.9

STATION	NUMBER	CITY	STATE	MONITOR METHOD	YEAR	NUMBER HOURS	10TH	30TH	50TH	70TH	90TH	95TH	99TH	MAX	ARITH MEAN	GEOM MEAN	GEOM STD DEV
							MICROGRAMS PER CUBIC METER										
5	4900001	YUB	CAL	1	1972	7825	9	9	38	38	56	75	113	188	32.0	22.3	2.3
5	4900001	YUB	CAL	1	1973	7908	19	19	38	38	75	75	132	244	37.0	31.2	1.7
5	4900001	YUB	CAL	1	1974	7902	19	19	38	38	75	94	150	376	38.0	31.1	1.8
6	580002	DEN	COL	3	1965	6988	38	56	56	75	113	113	188	526	68.0	59.7	1.7
6	580002	DEN	COL	3	1966	7771	38	38	56	75	94	113	188	620	64.0	53.8	1.9
6	580002	DEN	COL	3	1969	7321	9	38	56	75	94	113	207	639	61.0	47.7	2.2
6	580002	DEN	COL	3	1970	7370	9	56	56	75	113	150	207	658	71.0	56.1	2.2
6	580002	DEN	COL	3	1972	6759	9	38	56	75	132	169	282	602	72.0	52.9	2.3
6	580002	DEN	COL	2	1974	6646	38	56	75	94	132	169	282	790	86.0	71.9	1.9
6	580002	DEN	COL	3	1974	7169	35	53	81	100	150	182	310	769	89.0	73.8	1.9
7	680002	NEW	CON	1	1973	7528	9	23	34	45	68	79	120	196	38.0	30.7	1.9
7	680002	NEW	CON	1	1974	6861	9	19	26	38	53	60	90	169	30.0	24.5	1.9
9	20002	WAS	DIS	3	1962	7177	9	38	56	75	94	113	150	568	57.0	45.7	2.1
9	20002	WAS	DIS	3	1963	7176	9	38	56	75	113	132	188	414	65.0	52.6	2.0
9	20002	WAS	DIS	3	1964	7341	38	56	56	75	113	132	188	432	69.0	60.0	1.8
9	20002	WAS	DIS	3	1965	7487	38	56	56	75	113	113	169	432	65.0	56.9	1.8
9	20002	WAS	DIS	3	1967	7110	38	56	75	94	132	150	207	[illegible]	80.0	69.4	1.8
9	20003	WAS	DIS	3	1970	6888	38	75	94	113	169	207	262	564	90.0	79.1	2.1
9	20003	WAS	DIS	3	1971	7260	38	56	56	75	113	132	169	432	70.0	62.8	1.7
11	290001	ATL	GEO	2	1974	8499	47	60	85	103	141	160	216	470	93.0	82.0	1.6
9	20003	WAS	DIS	2	1974	6925	38	50	58	75	113	132	169	376	66.0	59.2	1.8
14	1220002	CHI	ILL	2	1974	8283	56	75	94	113	150	169	244	414	96.0	87.2	1.6
14	1220002	CHI	ILL	3	1962	7167	38	56	75	94	132	150	244	414	79.0	67.8	1.9
14	1220002	CHI	ILL	3	1963	7399	38	56	75	94	113	150	207	395	78.0	70.2	1.6
14	1220002	CHI	ILL	3	1964	7070	38	56	75	94	150	169	244	376	87.0	77.4	1.6
14	1220002	CHI	ILL	3	1965	7049	56	56	75	94	113	132	188	338	80.0	74.9	1.5
14	1220002	CHI	ILL	3	1966	6878	56	75	94	113	169	207	282	583	107.0	97.3	1.5
14	1220002	CHI	ILL	3	1967	6820	38	75	94	113	150	169	226	470	93.0	82.5	1.7
14	1220002	CHI	ILL	3	1968	6970	56	75	94	94	132	150	207	395	91.0	81.7	1.5
14	1220002	CHI	ILL	3	1969	7505	56	75	94	94	150	169	226	376	92.0	84.9	1.5
14	1220002	CHI	ILL	3	1970	7640	56	75	94	113	169	188	244	414	[illegible]	97.8	1.5
14	1220002	CHI	ILL	3	1972	7893	56	75	94	113	169	188	263	432	103.0	93.6	1.6
14	1220002	CHI	ILL	3	1973	6861	56	75	113	150	226	263	376	676	125.0	102.0	2.0
14	1220023	CHI	ILL	2	1974	8038	19	19	38	56	94	113	150	263	48.0	38.2	2.0
16	80008	ASH	KEN	1	1974	7382	23	39	56	83	132	171	205	756	71.0	56.0	2.0
18	2380011	LOU	KEN	2	1973	8249	38	56	75	94	122	150	197	517	70.0	60.5	1.7
18	2380011	LOU	KEN	2	1974	8678	38	56	75	103	132	160	197	329	84.0	75.2	1.6
18	2380017	LOU	KEN	2	1974	8663	19	38	56	75	113	150	188	320	66.0	56.0	2.0
18	3820001	LEX	KEN	1	1972	6809	9	38	53	75	113	135	197	402	59.0	44.7	2.3
18	3820001	LEX	KEN	1	1973	7789	9	41	60	79	105	122	162	312	63.0	50.6	2.1
18	3820001	LEX	KEN	1	1974	7348	47	66	75	103	132	150	188	357	86.0	78.2	1.6
18	3960006	[illegible]	KEN	1	1973	8152	9	9	9	9	19	38	56	248	13.0	10.9	1.5
18	3160006	[illegible]	KEN	1	1973	6982	28	53	73	103	160	197	290	639	87.0	70.0	2.0
19	[illegible]	NEW	LOU	3	1962	6974	38	56	75	75	113	150	188	414	74.0	63.2	1.9
19	[illegible]	NEW	LOU	3	1963	6904	9	9	38	38	56	75	98	207	31.0	22.3	2.3
21	120014	BAL	MAR	1	1973	6790	38	75	113	150	207	244	320	921	120.0	98.7	2.3
21	1460006	STL	MAR	1	1973	6799	9	56	94	132	188	226	320	790	97.0	65.9	2.8
22	2160005	SPR	MAS	2	1974	7827	38	75	94	132	207	244	338	526	111.0	90.3	2.0
23	1180020	DET	MIC	2	1974	7734	19	38	56	56	94	113	150	282	53.0	42.9	2.0
23	2840002	LSN	MIC	1	1974	7518	31	52	68	86	119	158	182	330	72.0	62.5	1.8

STATION NUMBER	CITY	STATE	MONITOR METHOD	YEAR	NUMBER HOURS	10TH	30TH	50TH	70TH	90TH	95TH	99TH	MAX	ARITH MEAN	GEOM MEAN	GEOM STD DEV
						MICROGRAMS PER CUBIC METER										
23 4760002	SAG	MIC	1	1974	7052	9	31	55	75	108	126	169	322	60.0	47.7	2.1
26 30001	AFT	MIS	1	1973	7904	24	56	79	103	152	177	233	457	85.0	67.0	2.2
26 200002	BEL	MIS	1	1973	7784	9	38	56	85	141	169	235	511	69.0	50.4	2.4
26 200002	BEL	MIS	1	1974	6678	9	36	55	83	135	171	312	444	69.0	49.1	2.4
26 1040001	CLA	MIS	1	1973	8022	9	43	60	86	133	162	201	464	70.0	53.7	2.3
26 4120001	STA	MIS	1	1973	7812	9	39	56	75	111	132	186	472	61.0	46.8	2.2
26 4120001	STA	MIS	1	1974	7365	23	43	68	94	139	171	243	451	70.0	59.2	2.2
26 4280002	STL	MIS	3	1965	7947	9	38	38	56	75	94	132	244	47.0	36.8	2.2
26 4280002	STL	MIS	3	1966	7261	38	38	56	75	113	132	169	376	64.0	53.5	2.0
26 4280002	STL	MIS	3	1967	7764	9	38	38	56	75	94	113	301	45.0	34.7	2.2
26 4280002	STL	MIS	3	1968	7213	9	38	38	56	75	94	132	338	43.0	32.6	2.3
26 4280002	STL	MIS	3	1971	7084	38	38	56	75	113	113	132	263	62.0	54.2	1.7
26 4280002	STL	MIS	2	1974	7071	19	56	56	94	113	150	207	414	71.0	59.1	1.9
26 4300006	STL	MIS	1	1973	8087	9	21	38	58	96	120	175	560	46.0	32.4	2.4
26 4300006	STL	MIS	1	1974	7250	9	30	53	79	128	165	293	656	65.0	44.4	2.5
29 320004	LAS	NEV	1	1972	7495	9	9	28	56	95	118	178	386	41.0	26.2	2.6
29 320004	LAS	NEV	1	1973	7329	9	9	37	56	90	109	186	286	44.0	30.6	2.4
29 480005	REN	NEV	4	1973	6505	23	38	55	75	113	132	207	382	63.0	50.9	2.0
29 480005	REN	NEV	4	1974	7162	19	28	47	66	94	122	188	630	57.0	43.6	2.0
31 180003	BAY	NEJ	3	1967	8108	38	66	88	115	158	177	269	532	95.0	80.5	1.8
31 180003	BAY	NEJ	3	1968	8218	39	68	96	120	160	184	250	585	99.0	85.8	1.6
31 180003	BAY	NEJ	3	1969	8019	41	71	98	128	167	196	254	487	103.0	89.9	1.7
31 180003	BAY	NEJ	3	1970	7735	26	53	75	100	137	164	241	692	81.0	66.1	2.0
31 180003	BAY	NEJ	3	1971	8209	33	49	73	98	141	171	246	504	80.0	62.9	2.2
31 180003	BAY	NEJ	3	1972	8007	28	60	81	100	147	175	239	568	85.0	69.8	2.0
31 180003	BAY	NEJ	3	1973	7497	30	56	83	107	154	182	252	442	89.0	73.3	2.0
31 180003	BAY	NEJ	3	1974	7638	9	34	55	79	117	139	196	305	61.0	46.0	2.1
31 720003	CAM	NEJ	3	1968	7903	36	60	81	103	143	165	227	506	87.0	75.0	1.8
31 720003	CAM	NEJ	3	1969	7477	34	58	79	103	147	167	255	1002	86.0	73.1	1.9
31 720003	CAM	NEJ	3	1970	7384	34	62	85	109	147	173	248	543	90.0	76.1	1.9
31 720003	CAM	NEJ	3	1971	8879	9	45	70	92	130	158	226	879	74.0	57.4	2.2
31 720003	CAM	NEJ	3	1972	8055	24	56	79	103	145	173	243	838	84.0	67.5	2.1
31 720003	CAM	NEJ	3	1973	8058	34	55	77	98	141	167	233	613	83.0	70.6	1.8
31 720003	CAM	NEJ	3	1974	7845	28	51	71	94	135	160	218	414	76.0	65.1	1.9
31 740001	CAR	NEJ	3	1967	7410	9	9	21	36	71	88	124	188	30.0	21.1	2.3
31 1300004	ELI	NEJ	3	1974	7817	45	71	90	115	160	186	259	575	99.0	87.4	1.7
31 3480002	NEW	NEJ	3	1967	8166	55	92	113	135	175	199	260	681	115.0	99.0	1.9
31 3480002	NEW	NEJ	3	1969	7290	64	90	111	135	180	204	286	453	118.0	108.2	1.5
31 3480002	NEW	NEJ	3	1970	7685	39	66	88	113	154	180	271	637	94.0	81.2	1.8
31 3480002	NEW	NEJ	3	1971	8004	41	68	92	122	182	222	320	688	105.0	87.8	1.9
31 3480002	NEW	NEJ	3	1972	6331	53	79	102	124	169	199	284	530	106.0	95.9	1.7
31 3480002	NEW	NEJ	3	1973	7982	56	86	111	141	197	233	316	617	121.0	107.9	1.6
31 3480002	NEW	NEJ	2	1974	6723	38	75	94	113	169	188	244	526	100.0	87.0	1.8
31 3480002	NEW	NEJ	3	1974	7593	41	66	86	113	156	180	252	632	94.0	81.8	1.8
31 4240002	PHI	NEJ	3	1972	8043	26	43	58	75	105	122	165	338	63.0	53.6	1.8
31 4240002	PHI	NEJ	3	1973	7769	26	43	58	75	107	124	167	357	64.0	54.5	1.8
31 4240002	PHI	NEJ	3	1974	7375	32	53	71	90	122	143	197	344	76.0	66.7	1.7
33 660005	BUF	NEY	1	1974	7333	9	32	53	77	124	150	205	320	62.0	44.8	2.4
33 660007	BUF	NEY	1	1974	7035	19	36	51	71	113	135	182	244	61.0	47.3	2.1
33 2480003	GLE	NEY	1	1974	7540	9	9	21	34	55	68	115	235	27.0	20.0	2.1

STATION NUMBER	CITY	STATE	MONITOR METHOD	YEAR	NUMBER HOURS	10TH	30TH	50TH	70TH	90TH	95TH	99TH	MAX	ARITH MEAN	GEOM MEAN	GEOM STD DEV
						MICROGRAMS PER CUBIC METER										
33 2900005	HEM	NEW	1	1974	7672	21	43	62	86	130	152	201	357	70.0	56.2	2.1
33 3500002	KIN	NEW	1	1974	7801	9	9	28	45	70	81	109	169	35.0	25.9	2.2
33 4100002	MAM	NEW	1	1974	7919	19	39	60	81	122	145	207	470	66.0	51.5	2.2
33 4680006	NEW	NEW	2	1974	6755	9	38	75	94	150	188	282	451	80.0	57.0	2.5
33 4680050	NEW	NEW	1	1974	8078	19	49	75	107	169	205	284	641	87.0	64.6	2.4
33 4680061	NEW	NEW	2	1974	8104	38	75	94	113	169	188	263	470	95.0	79.3	2.0
33 4780006	NIA	NEW	1	1974	7392	9	21	39	62	100	126	182	320	50.0	33.8	2.5
33 5680001	REN	NEW	1	1974	7572	9	9	28	43	73	86	115	184	35.0	26.0	2.2
33 5760004	ROC	NEW	1	1974	7239	9	28	45	62	88	103	145	[illegible]	49.0	37.9	2.2
33 6020003	SCH	NEW	1	1974	7322	9	19	30	45	71	83	113	169	35.0	26.6	2.2
33 6620005	SYR	NEW	1	1971	6953	9	9	26	47	66	107	160	372	38.0	24.9	2.5
33 6620005	SYR	NEW	1	1974	7676	9	34	51	70	100	115	150	321	55.0	43.1	2.1
33 6620011	SYR	NEW	1	1974	7914	32	49	62	77	103	117	150	244	66.0	59.0	1.6
33 6850004	UTI	NEW	1	1974	7656	9	32	43	56	83	94	122	244	47.0	39.0	2.0
36 60015	AKR	OHI	1	1973	6602	24	45	75	94	132	160	207	338	76.0	62.9	2.0
36 1220003	CIN	OHI	3	1962	6842	9	38	56	75	94	113	169	470	57.0	46.1	2.1
36 1220003	CIN	OHI	3	1963	7048	9	38	56	56	94	113	150	376	57.0	47.2	2.0
36 1220003	CIN	OHI	3	1964	7619	9	38	56	56	113	132	188	451	60.0	48.7	2.0
36 1220003	CIN	OHI	3	1965	7468	38	56	56	75	94	113	150	320	65.0	59.0	1.6
36 1220003	CIN	OHI	3	1966	6648	38	56	56	75	113	132	188	451	69.0	58.6	1.8
36 1220003	CIN	OHI	3	1967	6805	38	38	56	56	75	94	132	451	53.0	48.3	1.8
36 1220019	CIN	OHI	2	1974	8028	19	38	38	56	94	113	132	320	50.0	41.6	1.9
36 1460002	POR	ORE	1	1970	8200	19	38	56	56	75	94	150	451	53.0	46.7	1.7
38 1460002	POR	ORE	1	1971	8288	19	38	38	56	75	94	132	284	47.0	40.8	1.7
38 1460002	POR	ORE	1	1972	8060	19	38	38	56	75	94	131	357	47.0	40.9	1.7
38 1460002	POR	ORE	1	1973	8051	19	38	56	75	94	94	150	301	55.0	47.2	1.8
38 1460002	POR	ORE	1	1974	8055	9	19	38	56	94	112	150	357	47.0	37.4	2.0
39 4660107	LAN	PEN	2	1973	6725	9	19	30	38	56	64	79	158	31.0	25.4	1.9
39 7140002	PHI	PEN	3	1963	6753	38	56	75	75	113	150	226	602	73.0	59.8	2.0
39 7140002	PHI	PEN	3	1964	6705	38	56	56	75	113	150	207	489	71.0	59.5	1.9
39 7140002	PHI	PEN	3	1965	6842	38	56	56	75	113	132	169	376	69.0	58.7	1.8
39 7140002	PHI	PEN	3	1966	7826	38	56	56	75	132	150	207	432	73.0	63.2	1.8
39 7140002	PHI	PEN	3	1967	7559	38	56	75	94	132	150	207	432	80.0	69.3	1.8
39 7140002	PHI	PEN	3	1968	6887	38	56	56	94	132	150	226	376	74.0	61.7	1.9
39 7140002	PHI	PEN	3	1969	7253	38	56	56	75	113	132	169	263	69.0	59.0	1.9
39 7140002	PHI	PEN	3	1970	7105	38	75	75	113	150	169	244	395	91.0	80.5	1.7
39 7140002	PHI	PEN	2	1973	6644	38	56	56	75	132	150	226	545	72.0	60.3	1.9
39 7140002	PHI	PEN	2	1974	6634	38	56	75	94	132	150	188	432	74.0	62.9	1.9
39 7140004	PHI	PEN	1	1972	8598	38	56	75	94	132	150	207	470	85.0	72.6	1.7
39 8040006	SCR	PEN	2	1974	6793	9	9	26	41	64	71	94	150	31.0	24.0	2.1
41 300005	PRO	RHO	3	1972	7808	38	66	85	113	160	188	254	489	95.0	81.8	1.8
41 300005	PRO	RHO	3	1973	7366	33	47	66	89	122	150	188	329	75.0	65.4	1.8
41 300007	PRO	RHO	3	1972	6956	9	47	66	79	109	126	171	301	66.0	52.5	2.2
41 300007	PRO	RHO	3	1973	7953	38	53	66	79	109	128	167	244	70.0	63.7	1.6
41 300007	PRO	RHO	3	1974	6834	32	53	71	88	124	181	168	385	75.0	66.2	1.7
44 2340027	CHA	TEN	4	1974	6238	9	9	9	9	38	56	94	338	16.0	12.7	1.8
44 5280005	STE	TEN	1	1973	6926	9	9	9	9	9	19	75	226	12.0	10.3	1.6
44 5280005	STE	TEN	1	1974	6683	9	9	9	19	19	38	56	207	15.0	12.8	1.7
46 920001	SAL	UTA	2	1974	7762	19	38	56	75	113	150	226	395	68.0	53.4	2.1
48 80009	ALE	VIR	1	1974	7376	28	47	66	75	113	132	169	282	68.0	58.6	1.8

APPENDIX B

DERIVATION OF FORMULAS FOR DISTRIBUTION OF MAXIMA

General

Let an individual hourly concentration, X, have a cumulative frequency distribution

$$P(C) = \text{probability that } X < C \quad .$$

Let C_m be the maximum of a sample of size N, drawn independently from the distribution P(C), i.e.

$$C_m = \max\,(C_1, \ldots, C_N) \; .$$

Then, the cumulative frequency distribution for C_m is

$$\begin{aligned} M(C_m) &= \text{probability that all } C_1, \ldots, C_N \text{ are less than } C_m \\ &= [P(C_m)]^N \qquad \text{(B-1)} \end{aligned}$$

For large N,

$$M(C_m) \approx e^{-N[1 - P(C_m)]} \; . \qquad \text{(B-2)}$$

Lognormal Distribution

For the lognormal distribution, P(C) equals $F(\ell n C)$, where F is the cumulative frequency distribution for the normal distribution. The cumulative frequency distribution for the maxima is

$$M(C_m) = e^{-N[1 - F(\ell n C)]} \qquad \text{(B-3)}$$

Gamma Distribution

For the Gamma distribution, P(C) equals G(C), where

$$G(C) = \frac{1}{\Gamma(\alpha)} \int_0^C \frac{u^{\alpha-1}}{\beta^{\alpha}} e^{-u/\beta}\, du \qquad \text{(B-4)}$$

$$= \frac{1}{\Gamma(\alpha)} \int_0^{C/\beta} v^{\alpha-1} e^{-v} \, dv \, .$$

Changing variables to t = C/β,

$$G(C) = \frac{1}{\Gamma(\alpha)} \int_0^{t} v^{\alpha-1} e^{-v} \, dv$$

$$= 1 - \frac{1}{\Gamma(\alpha)} \int_t^{\infty} v^{\alpha-1} e^{-v} \, dv. \tag{B-5}$$

Since we are examining maximal values, we can assume t is large. For large t,

$$G(C) \sim 1 - \frac{1}{\Gamma(\alpha)} t^{\alpha-1} e^{-t} \, .$$

Using Equation (B-2), the distribution of the maximum is

$$M(C_m) = e^{\frac{-N}{\Gamma(\alpha)} t^{\alpha-1} e^{-t}} \tag{B-6}$$

where $t = C_m/\beta$.

To make the distribution of the maxima independent of both β and α, let

$$S = t - \Delta = C_m / \beta - \Delta \tag{B-7}$$

where

$$\frac{N}{\Gamma(\alpha)} \Delta^{\alpha-1} e^{-\Delta} = 1 \, . \tag{B-8}$$

Then, substituting (B-7) and (B-8) into Equation (B-6) yields

$$M(C_m) = \exp\left[-\left(\frac{s}{\Delta} + 1\right)^{\alpha-1} e^{-s}\right] \tag{B-9}$$

For the data base in question, α tends to be near to one, and s tends to be small compared with Δ. Thus, we use the approximation

$$\left(\frac{s}{\Delta} + 1\right)^{\alpha-1} \approx 1\ . \tag{B-10}$$

With this approximation, the formula for the distribution of maxima from Gamma distribution is

$$M(C_m) = e^{-e^{-s}} \tag{B-11}$$

where

$$s = C_m / \beta - \Delta$$

and Δ is the solution to

$$\frac{N}{\Gamma(\alpha)}\ \Delta^{\alpha-1}\ e^{-\Delta} = 1\ .$$

APPENDIX C

DATA FOR CHARACTERIZING PRESENT NO_2 AIR QUALITY

STATION	YEARS OF DATA	ARITHMETIC MEAN "m" (pphm)	90TH PERCENTILE "C_{90}" (pphm)	YEARLY MAX ONE-HOUR CONC. "X_m" (pphm)	MAX-TO-MEAN RATIO $X_m \div m$
1. Phoenix, AZ (002A01)	73	1.9	5.0	22.7	12.2
2. Anaheim, CA (001I01)	72,73,74	5.1	9.0	40.7	7.9
3. Azusa, CA (002I01)	72,73,74	6.2	11.4	41.0	6.6
4. Bakersfield, CA (003F01)	72,73,74	3.0	5.7	14.7	5.0
5. Barstow, CA (001I01)	74	4.0	8.0	47.7	12.0
6. Burbank, CA (002I01)	74	7.1	13.0	35.4	5.0
7. Camarillo, CA (001I01)	72,73	3.0	5.5	20.8	6.9
8. Chico, CA (001F01)	72,73,74	1.8	4.0	10.6	5.8
9. Chino, CA (001I01)	74	3.4	7.0	37.7	11.1
10. Concord, CA (001I01)	74	2.7	5.0	20.5	7.5
11. Costa Mesa, CA (001I01)	74	3.0	7.0	30.8	10.2
12. El Cajon, CA (001I01)	72,73	3.0	5.5	22.2	7.5
13. Eureka, CA (002F01)	73	1.7	3.0	10.3	6.0

STATION	YEARS OF DATA	ARITHMETIC MEAN "m" (pphm)	90TH PERCENTILE "C_{90}" (pphm)	YEARLY MAX ONE-HOUR CONC. "X_m" (pphm)	MAX-TO-MEAN RATIO $X_m \div m$
14. Fresno, CA (002F01)	72,73,74	2.7	5.0	20.0	7.4
15. Indio, CA (001I01)	72,73,74	1.7	3.3	11.2	6.8
16. La Habra, CA (001I01)	72,73,74	5.6	9.7	42.9	7.7
17. Lancaster, CA (001I01)	72,73,74	1.4	2.7	9.4	6.8
18. Lennox, CA (001I01)	72,73,74	6.4	11.0	40.7	6.4
19. Livermore, CA (002I01)	72,73,74	3.3	5.7	17.2	5.2
20. Long Beach, CA (002I01)	74	6.7	12.0	37.7	5.6
21. Los Alamitos, CA (001I01)	72	4.7	9.0	36.3	7.8
22. Los Angeles (Downtown), CA (001I01)	72,73,74	7.3	12.3	54.6	7.6
23. Los Angeles (Westwood), CA (002I01)	72,73,74	6.8	12.3	55.8	8.1
24. Los Angeles (Reseda) (001I01)	72,73,74	6.3	11.7	36.7	5.8
25. Lynwood, CA (001I01)	74	5.5	9.0	37.7	6.9

STATION	YEARS OF DATA	ARITHMETIC MEAN "m" (pphm)	90TH PERCENTILE "C_{90}" (pphm)	YEARLY MAX ONE-HOUR CONC. "X_m" (pphm)	MAX-TO-MEAN RATIO $X_m \div m$
26. Modesto, CA (001I01)	72,73,74	2.7	4.3	14.2	5.2
27. Monterey, CA (001I01)	72,73,74	1.5	2.7	10.8	7.3
28. Napa, CA (003I01)	74	2.6	4.0	14.1	5.4
29. Newhall, CA (001I01)	72,73,74	3.6	6.7	23.0	6.3
30. Norco, CA (001I01)	74	2.8	5.0	22.4	7.9
31. Oakland, CA (003G01)	72,73,74	3.5	6.0	22.7	6.6
32. Ojai, CA (001I01)	72	1.5	4.0	19.9	13.4
33. Palm Springs, CA (001I01)	72,73,74	1.5	3.0	8.8	6.1
34. Pasadena, CA (004I01)	74	7.3	12.0	47.7	6.5
35. Pittsburg, CA (001I01)	72,73,74	1.9	3.7	10.2	5.5
36. Pomona, CA (001I01)	74	6.9	11.0	34.3	5.0
37. Redding, CA (002F01)	72,73,74	1.8	3.0	9.9	5.4
38. Redlands, CA (001I01)	72,73,74	4.0	7.7	24.7	6.2

STATION	YEARS OF DATA	ARITHMETIC MEAN "m" (pphm)	90TH PERCENTILE "C_{90}" (pphm)	YEARLY MAX ONE-HOUR CONC. "X_m" (pphm)	MAX-TO-MEAN RATIO $X_m \div m$
39. Redwood City, CA (001I01)	72,73,74	2.7	5.0	21.4	8.0
40. Richmond, CA (003I01)	74	2.8	5.0	14.2	5.1
41. Riverside, CA (003F01)	74	5.0	9.0	25.5	5.1
42. Rubidoux, CA (001I01)	74	2.7	5.0	20.3	7.6
43. Sacramento, CA (003F01)	72,73,74	2.8	4.7	18.0	6.5
44. Salinas, CA (001I01)	72,73,74	2.2	4.0	13.5	6.2
45. San Bernardino, CA (001I01)	72,73,74	4.3	7.7	32.0	7.3
46. San Diego, CA (004I01)	74	2.7	6.0	25.6	9.6
47. San Francisco, CA (003I01)	72,73,74	3.3	5.0	23.9	7.2
48. San Jose, CA (004A05)	73,74	3.8	6.5	30.2	8.0
49. San Luis Obispo, CA (001F01)	72,73,74	2.1	4.0	10.9	5.3
50. San Rafael, CA (001I01)	72,73,74	2.8	4.7	16.9	6.0
51. Santa Barbara, CA (002F01)	72	3.6	6.0	16.4	4.6
52. Santa Barbara, CA (004F01)	72,73,74	3.1	5.0	20.5	6.6

STATION	YEARS OF DATA	ARITHMETIC MEAN "m" (pphm)	90TH PERCENTILE "C_{90}" (pphm)	YEARLY MAX ONE-HOUR CONC. "X_m" (pphm)	MAX-TO-MEAN RATIO $X_m \div m$
53. Santa Cruz, CA (001I01)	72,73,74	1.5	2.3	10.5	6.9
54. Santa Rosa, CA (002I01)	74	2.0	4.0	15.2	7.8
55. Stockton, CA (002F01)	72,73,74	2.7	4.3	15.8	5.8
56. Sunnyvale, CA (001I01)	74	4.1	7.0	31.7	7.7
57. Upland, CA (003I01)	74	6.0	11.0	39.7	6.7
58. Upland, CA (004F01)	74	4.9	9.0	28.6	5.8
59. Vallejo, CA (003I01)	74	2.6	4.0	14.2	5.4
60. Victorville, CA (001I01)	74	3.7	8.0	23.5	6.3
61. Visalia, CA (001F01)	72,73,74	2.3	4.0	12.6	5.6
62. Whittier, CA (001I01)	72,73,74	6.5	11.3	50.6	7.8
63. Yuba City, CA (001F01)	72,73,74	1.9	3.7	14.6	7.6
64. Denver, CO (002A05)	74,72,74	4.4	7.3	40.2	9.2
65. New Britain, CT (002F01)	73,74	1.8	3.2	10.1	5.6

STATION	YEARS OF DATA	ARITHMETIC MEAN "m" (pphm)	90TH PERCENTILE "C_{90}" (pphm)	YEARLY MAX ONE-HOUR CONC. "X_m" (pphm)	MAX-TO-MEAN RATIO $X_m \div m$
66. Washington, DC (003A05)	74	3.6	6.0	17.1	4.7
67. Atlanta, GA (001A05)	74	4.8	7.5	25.1	5.2
68. Chicago, IL (002A05)	74,72,73	5.7	9.7	27.7	4.8
69. Chicago, IL (023A05)	74	2.6	5.0	14.2	5.6
70. Ashland, KY (008F01)	74	3.8	7.0	41.6	11.0
71. Louisville, KY (011G01)	73,74	4.3	6.8	22.6	5.3
72. Louisville, KY (017A05)	74	3.6	6.0	17.1	4.7
73. Newport, KY (001F01)	72,73,74	3.7	6.2	19.7	5.5
74. Ohio, KY (006N02)	73	0.7	1.0	13.1	18.9
75. Owensboro, KY (008F01)	73	4.6	8.5	35.5	7.7
76. Baltimore, MD (018F01)	73	6.4	11.0	51.9	8.1
77. Silver Spring, MD (006F01)	73	5.2	10.0	45.1	8.8

STATION	YEARS OF DATA	ARITHMETIC MEAN "m" (pphm)	90TH PERCENTILE "C_{90}" (pphm)	YEARLY MAX ONE-HOUR CONC. "X_m" (pphm)	MAX-TO-MEAN RATIO $X_m \div m$
78. Springfield, MA (005A05)	74	5.9	11.0	28.6	4.9
79. Detroit, MI (020A05)	74	2.8	5.0	15.4	5.5
80. Lansing, MI (002F01)	74	3.8	6.3	18.0	4.7
81. Saginaw, MI (002F01)	74	3.2	5.7	17.9	5.6
82. Afton, MO (001G01)	73	4.5	8.1	24.9	5.5
83. BelleFontaine Neighbors, MO (002G01)	73,74	3.7	7.3	26.6	7.3
84. Clayton, MO (001G01)	73	3.7	7.1	25.2	6.8
85. St. Ann, MO (001G01)	73,74	3.6	6.7	25.4	7.1
86. St. Louis, MO (002A10)	74	3.8	6.0	22.9	6.1
87. St. Louis, MO (006G01)	73,74	3.0	6.0	33.6	11.5
88. Las Vegas, NV (009G01)	72,73	2.3	4.9	18.8	8.4
89. Reno, NV (005I01)	73,74	3.2	5.5	26.6	8.5

STATION	YEARS OF DATA	ARITHMETIC MEAN "m" (pphm)	90TH PERCENTILE "C_{90}" (pphm)	YEARLY MAX ONE-HOUR CONC. "X_m" (pphm)	MAX-TO-MEAN RATIO $X_m \div m$
90. Bayonne, NJ (003F01)	72,73,74	4.2	7.4	23.9	5.7
91. Camden, NJ (003F01)	72,73,74	4.3	7.4	26.4	6.1
92. Elizabeth, NJ (004F01)	74	5.3	8.5	31.1	5.9
93. Newark, NJ (002F01)	72,73,74	5.6	9.2	31.3	5.6
94. Phillipsburg, NJ (002F01)	72,73,74	3.6	5.9	18.8	5.3
95. Buffalo, NY (005F01)	74	3.3	6.6	17.8	5.4
96. Buffalo, NY (007F01)	74	3.2	6.0	13.6	4.3
97. Glens Falls, NY (003F01)	74	1.4	2.9	12.9	9.0
98. Hempstead, NY (005F01)	74	3.7	6.9	19.5	5.3
99. Kingston, NY (002F01)	74	1.9	3.7	9.2	4.8
100. Mamaroneck, NY (002F01)	74	3.5	6.5	25.6	7.3
101. New York City, NY (006A05)	74	4.3	8.0	25.6	6.0
102. New York City, NY (050F01)	74	4.6	9.0	34.8	7.5

STATION	YEARS OF DATA	ARITHMETIC MEAN "m" (pphm)	90TH PERCENTILE "C_{90}" (pphm)	YEARLY MAX ONE-HOUR CONC. "X_m" (pphm)	MAX.-TO-MEAN RATIO $X_m \div m$
103. New York City, NY (061A05)	74	5.1	9.0	25.4	5.0
104. Niagara Falls, NY (006F01)	74	2.7	5.3	17.8	6.6
105. Rensselaer, NY (001F01)	74	1.9	3.9	10.2	5.5
106. Rochester, NY (004F01)	74	2.6	4.7	11.5	4.4
107. Schenectady, NY (003F01)	74	1.9	3.8	9.4	5.0
108. Syracuse, NY (005F01)	74	2.9	5.3	17.6	6.0
109. Syracuse, NY (011F01)	74	3.5	5.5	13.3	3.8
110. Utica, NY (004F01)	74	2.5	4.4	13.3	5.3
111. Akron, OH (013H01)	73	4.0	7.0	18.9	4.7
112. Cincinnati, OH (019A05)	74	2.7	5.0	17.3	6.5
113. Portland, OR (002F01)	72,73,74	2.6	4.7	18.3	7.0
114. Lancaster City, PA (007F01)	74	1.7	3.0	8.8	5.3
115. Philadelphia, PA (002A05)	73,74	3.9	7.0	27.2	7.0

STATION	YEARS OF DATA	ARITHMETIC MEAN "m" (pphm)	90TH PERCENTILE "C_{90}" (pphm)	YEARLY MAX ONE-HOUR CONC. "X_m" (pphm)	MAX-TO-MEAN RATIO $X_m \div m$
116. Philadelphia, PA (004H01)	72	4.5	7.0	25.1	5.6
117. Scranton, PA (006F01)	74	1.7	3.4	8.4	5.1
118. Providence, RI (005F01)	72,73	4.5	7.5	22.3	4.9
119. Providence, RI (007A05)	72,73,74	3.7	6.1	17.1	4.6
120. Memphis, TN (027N02)	74	0.9	2.0	18.2	21.4
121. Stewart, TN (005N02)	73,74	0.7	0.7	11.9	16.8
122. Salt Lake City, UT (001A05)	74	3.6	6.0	21.6	6.0
123. Alexandria, VA (009H01)	74	3.6	6.0	15.4	4.3

APPENDIX D

SUMMARY OF DAYTIME AND NIGHTTIME REGRESSION MODELS FOR LENNOX, AZUSA, POMONA, DENVER, CHICAGO, HOUSTON/MAE, AND HOUSTON/ALDINE

Table D-1 Summary of Daytime Regressions for Lennox

1. Regression of Daytime NO_2 vs. NO_25 and INTNO

$$\begin{matrix} DPKNO_2 \\ \text{or} \\ DAVNO_2 \end{matrix} = A + B_1 \cdot NO_25 + B_2 \cdot INTNO$$

	TOTAL CORR. COEF.	% VARIANCE EXPLAINED	A	B_1	B_2
WINTER					
$DPKNO_2$	.76	57%	2.4	.70	.14
$DAVNO_2$	.78	61%	2.2	.46	.08
SUMMER					
$DPKNO_2$	.74	55%	3.4	.70	.24
$DAVNO_2$	.78	60%	2.7	.47	.13

2. Estimation of the Hydrocarbon Effect

$$\begin{matrix} DPKNO_2 \\ \text{or} \\ DAVNO_2 \end{matrix} = (A + C_0) + B_1 \cdot NO_25 + INTNO \cdot (B_2' + C_1 \cdot RATIO + C_2 \cdot NMHCPR)$$

	TOTAL CORR. COEF.	% VARIANCE EXPLAINED	$A + C_0$	B_1	B_2'	C_1	C_2
WINTER							
$DPKNO_2$	.77	59%	2.6	.70	.08	.011	*
$DAVNO_2$	.78	62%	2.3	.46	.06	.004	*
SUMMER							
$DPKNO_2$	.77	59%	3.5	.70	.09	.021	.00011
$DAVNO_2$	.78	61%	2.7	.47	.10	.005	*

*Not significant from zero at 95% confidence level.

Note: NMHCPR = (HC69 - 100 pphm)/2

Units of all variables are in pphm.

Table D-2 Summary of Nighttime Regressions for Lennox

1. Regression of Nighttime NO_2 vs. $NO_2 16$, NITENO, and O_3AFT·NITENO

$$\left.\begin{array}{c}\text{NPKNO}_2\\ \text{or}\\ \text{NAVNO}_2\end{array}\right\} = A + B_1 \cdot NO_2 16 + B_2 \cdot NITENO + B_3 \cdot NITENO \cdot O_3\ AFT$$

	TOTAL CORR. COEF.	% VARIANCE EXPLAINED	A	B_1	B_2	B_3
WINTER						
$NPKNO_2$	.81	66%	2.4	.77	.04	.026
$NAVNO_2$	.75	56%	2.4	.48	*	.020
SUMMER						
$NPKNO_2$	.80	65%	2.0	.77	*	.048
$NAVNO_2$	.74	55%	1.5	.48	.06	.021

*Not significant from zero at 95% confidence level.

2. Dependence of Afternoon NO_2 ($NO_2 16$) on NMHC/NO_x Ratio

WINTER: $NO_2 16 = 8.3 \text{ pphm } (1 - .028 \frac{NMHCPR}{NOX69})$

SUMMER: $NO_2 16 = 6.4 \text{ pphm } (1 - .024 \frac{NMHCPR}{NOX69})$

Note: Units of all variables are in pphm.

Table D-3 Summary of Daytime Regressions for Azusa

1. Regression of Daytime NO_2 vs. NO_25 and INTNO

$$\left.\begin{array}{c}DPKNO_2\\ \text{or}\\ DAVNO_2\end{array}\right. = A + B_1 \cdot NO_25 + B_2 \cdot INTNO$$

	TOTAL CORR. COEF.	% VARIANCE EXPLAINED	A	B_1	B_2
WINTER					
$DPKNO_2$	.87	75%	1.6	1.05	.52
$DAVNO_2$	.88	78%	1.0	.78	.33
SUMMER					
$DPKNO_2$	.88	78%	1.4	.92	.57
$DAVNO_2$	.85	73%	1.7	.56	.30

2. Estimation of the Hydrocarbon Effect

$$\left.\begin{array}{c}DPKNO_2\\ \text{or}\\ DAVNO_2\end{array}\right. = (A + C_0) + B_1 \cdot NO_25 + INTNO \cdot (B_2' + C_1 \cdot RATIO + C_2 \cdot NMHCPR)$$

	TOTAL CORR. COEF.	% VARIANCE EXPLAINED	$A + C_0$	B_1	B_2'	C_1	C_2
WINTER							
$DPKNO_2$	.88	77%	1.7	1.05	.21	.010	.00099
$DAVNO_2$	.89	79%	1.1	.78	.14	.006	.00060
SUMMER							
$DPKNO_2$	.88	78%	1.4	.92	.57	*	*
$DAVNO_2$	.86	73%	1.7	.56	.32	*	-.00016

*Not significant from zero at 95% confidence level.

Note: NMHCPR = (HC69-100 pphm)/2

Units of all variables are in pphm.

Table D-4 Summary of Nighttime Regressions for Azusa

1. Regression of Nighttime NO_2 vs. NO_216, NITENO, and $O_3AFT \cdot NITENO$

$$\left.\begin{array}{c}NPKNO_2\\ \text{or}\\ NAVNO_2\end{array}\right. = A + B_1 \cdot NO_216 + B_2 \cdot NITENO + B_3 \cdot NITENO \cdot \dot{O}_3\ AFT$$

	TOTAL CORR. COEF.	% VARIANCE EXPLAINED	A	B_1	B_2	B_3
WINTER						
$NPKNO_2$	.91	84%	1.5	.82	.44	.042
$NAVNO_2$	.90	80%	0.9	.48	.16	.035
SUMMER						
$NPKNO_2$	.74	54%	2.7	.82	.34	.042
$NAVNO_2$	.76	58%	1.7	.61	.12	.033

2. Dependence of Afternoon NO_2 (NO_216) on $NMHC/NO_x$ Ratio

$$\underline{\text{WINTER}}:\ NO_216 = 9.9\ \text{pphm}\ \left(1 - .017\ \frac{NMHCPR}{NOX69}\right)$$

$$\underline{\text{SUMMER}}:\ NO_216 = 5.8\ \text{pphm}\ \left(1 - .011\ \frac{NMHCPR}{NOX69}\right)$$

Note: Units of all variables are in pphm.

Table D-5 Summary of Daytime Regressions for Pomona

1. Regression of Daytime NO_2 vs. NO_25 and INTNO

$DPKNO_2$

or $= A + B_1 \cdot NO_25 + B_2 \cdot INTNO$

$DAVNO_2$

	TOTAL CORR. COEF.	% VARIANCE EXPLAINED	A	B_1	B_2
WINTER					
$DPKNO_2$	.83	69%	.5	1.14	.12
$DAVNO_2$	.84	70%	.7	.87	.07
SUMMER					
$DPKNO_2$	.85	73%	2.0	.90	.30
$DAVNO_2$	.85	73%	2.1	.58	.19

2. Estimation of the Hydrocarbon Effect

$DPKNO_2$

or $= (A + C_0) + B_1 \cdot NO_25 + INTNO \cdot (B_2' + C_1 \cdot RATIO + C_2 \cdot NMHCPR)$

$DAVNO_2$

	TOTAL CORR. COEF.	% VARIANCE EXPLAINED	$A + C_0$	B_1	B_2'	C_1	C_2
WINTER							
$DPKNO_2$	.86	74%	.5	1.14	-.14	.020	.00100
$DAVNO_2$	.86	74%	.8	.87	-.09	.012	.00065
SUMMER							
$DPKNO_2$	.87	75%	2.2	.90	.03	.018	.00119
$DAVNO_2$	.86	74%	2.2	.58	.05	.010	.00056

Note: NMHCPR = (HC69 - 100 pphm)/2

Units of all variables are in pphm.

Table D-6 Summary of Nighttime Regressions for Pomona

1. Regression of Nighttime NO_2 vs. NO_216, NITENO, and O_3AFT·NITENO

$$\left.\begin{array}{c}\text{NPKNO}_2\\ \text{or}\\ \text{NAVNO}_2\end{array}\right. = A + B_1 \cdot NO_216 + B_2 \cdot NITENO + B_3 \cdot NITENO \cdot O_3\ AFT$$

	TOTAL CORR. COEF.	% VARIANCE EXPLAINED	A	B_1	B_2	B_3
WINTER						
$NPKNO_2$	.87	75%	1.6	.85	*	.067
$NAVNO_2$	.84	71%	2.4	.50	-.05	.043
SUMMER						
$NPKNO_2$	.71	50%	3.1	.81	*	.058
$NAVNO_2$	.71	51%	2.4	.57	*	.041

*Not significant from zero at 95% confidence level.

2. Dependence of Afternoon NO_2 (NO_216) on $NMHC/NO_x$ Ratio

WINTER: $NO_216 = 9.9\ \text{pphm}\ (1 - .027\ \frac{NMHCPR}{NOX79})$

SUMMER: $NO_216 = 7.3\ \text{pphm}\ (1 - .018\ \frac{NMHCPR}{NOX79})$

Note: Units of all variables are in pphm.

Table D-7 Summary of Daytime Regressions for Denver

1. Regression of Daytime NO_2 vs. NO_25 and INTNO

$$\left.\begin{array}{c}DPKNO_2\\ \text{or}\\ DAVNO_2\end{array}\right. = A + B_1 \cdot NO_25 + B_2 \cdot INTNO$$

	TOTAL CORR. COEF.	% VARIANCE EXPLAINED	A	B_1	B_2
WINTER					
$DPKNO_2$	.65	42%	1.5	.71	.32
$DAVNO_2$	.70	49%	1.3	.41	.17
SUMMER					
$DPKNO_2$	.70	50%	1.5	.58	.37
$DAVNO_2$	.72	51%	1.1	.33	.18

2. Estimation of the Hydrocarbon Effect

$$\left.\begin{array}{c}DPKNO_2\\ \text{or}\\ DAVNO_2\end{array}\right. = (A + C_0) + B_1 \cdot NO_25 + INTNO \cdot (B_2' + C_1 \cdot RATIO + C_2 \cdot NMHCPR)$$

	TOTAL CORR. COEF.	% VARIANCE EXPLAINED	$A + C_0$	B_1	B_2'	C_1	C_2
WINTER							
$DPKNO_2$	.66	44%	1.6	.71	.23	.010	*
$DAVNO_2$	.73	53%	1.6	.41	.23	-.005	-.00016
SUMMER							
$DPKNO_2$	.71	51%	1.6	.58	.28	.007	*
$DAVNO_2$	.73	53%	1.3	.33	.12	.004	*

*Not significant from zero at 95% confidence level.

Note: For Denver, NMHCPR is defined as .6(HC69-135 pphm). This formula results from regressing the Denver NMHC69 measurements against the Denver HC69 measurements.

Units of all variables are in pphm.

Table D-8 Summary of Nighttime Regressions for Denver

1. Regression of Nighttime NO_2 vs. $NO_2 16$, NITENO, and $O_3AFT \cdot NITENO$

$$\left.\begin{array}{c} NPKNO_2 \\ \text{or} \\ NAVNO_2 \end{array}\right. = A + B_1 \cdot NO_2 16 + B_2 \cdot NITENO + B_3 \cdot NITENO \cdot \dot{O}_3\ AFT$$

	TOTAL CORR. COEF.	% VARIANCE EXPLAINED	A	B_1	B_2	B_3
WINTER						
$NPKNO_2$	.82	67%	2.0	.73	.16	*
$NAVNO_2$	.78	60%	2.0	.35	.10	*
SUMMER						
$NPKNO_2$	.50	25%	3.2	.66	*	*
$NAVNO_2$	.55	30%	1.7	.39	.09	*

*Not significant from zero at 95% confidence level.

2. Dependence of Afternoon NO_2 ($NO_2 16$) on $NMHC/NO_x$ Ratio

$$\underline{\text{WINTER}}:\ NO_2 16 = 7.56 \text{ pphm } \left(1 - .044\ \frac{NMHCPR}{NOX79}\right)$$

$$\underline{\text{SUMMER}}:\ NO_2 16 = 2.70 \text{ pphm } \left(1 - .007\ \frac{NMHCPR}{NOX69}\right)$$

Note: Units of all variables are in pphm.

Table D-9 Summary of Daytime Regressions for Chicago

1. Regression of Daytime NO_2 vs. NO_25 and INTNO

$DPKNO_2$

or $= A + B_1 \cdot NO_25 + B_2 \cdot INTNO$

$DAVNO_2$

	TOTAL CORR. COEF.	% VARIANCE EXPLAINED	A	B_1	B_2
WINTER					
$DPKNO_2$	.65	43%	1.7	.86	.07
$DAVNO_2$	.74	54%	1.5	.66	.05
SUMMER					
$DPKNO_2$	.70	49%	2.0	.98	.14
$DAVNO_2$	.78	60%	1.3	.82	.11

2. Estimation of the Hydrocarbon Effect

$DPKNO_2$

or $= (A + C_0) + B_1 \cdot NO_25 + INTNO \cdot (B_2' + C_1 \cdot RATIO + C_2 \cdot NMHCPR)$

$DAVNO_2$

	TOTAL CORR. COEF.	% VARIANCE EXPLAINED	$A + C_0$	B_1	B_2'	C_1	C_2
WINTER							
$DPKNO_2$	.70	49%	1.6	.86	-.01	.029	*
$DAVNO_2$	.76	58%	1.5	.66	.01	.015	*
SUMMER							
$DPKNO_2$	.70	49%	2.0	.98	.14	*	*
$DAVNO_2$	.78	60%	1.3	.82	.11	*	*

*Not significant from zero at 95% confidence level.

Note: NMHCPR = .57(HC69-144 pphm)

Units of all variables are in pphm.

Table D-10 Summary of Nighttime Regressions for Chicago

1. Regression of Nighttime NO_2 vs. $NO_2$16, NITENO, and O_3AFT·NITENO

$$\begin{array}{l} NPKNO_2 \\ \text{or} \\ NAVNO_2 \end{array} = A + B_1 \cdot NO_2 16 + B_2 \cdot NITENO + B_3 \cdot NITENO \cdot O_3\,AFT$$

	TOTAL CORR. COEF.	% VARIANCE EXPLAINED	A	B_1	B_2	B_3
WINTER						
$NPKNO_2$	.86	75%	1.0	.78	.03	-.007
$NAVNO_2$	.80	63%	1.3	.49	.04	-.006
SUMMER						
$NPKNO_2$	.90	80%	1.3	.89	*	.014
$NAVNO_2$	.84	70%	1.4	.58	.02	.008

*Not significant from zero at 95% confidence level.

2. Dependence of Afternoon NO_2 ($NO_2$16) on $NMHC/NO_x$ Ratio

WINTER: $NO_2 16$ independent of $\frac{NMHCPR}{NOX79}$

SUMMER: $NO_2 16 = 9.6 \text{ pphm } (1 - .034 \frac{NMHCPR}{NOX79})$

Note: Units of all variables are in pphm.

Table D-11 Summary of Daytime Regressions for Houston/Mae

1. Regression of Daytime NO_2 vs. NO_25 and INTNO

$$\left.\begin{array}{c} DPKNO_2 \\ \text{or} \\ DAVNO_2 \end{array}\right. = A + B_1 \cdot NO_25 + B_2 \cdot INTNO$$

	TOTAL CORR. COEF.	% VARIANCE EXPLAINED	A	B_1	B_2
WINTER					
$DPKNO_2$	.77	60%	.93	.86	.15
$DAVNO_2$	.80	65%	.55	.48	.074
SUMMER					
$DPKNO_2$	.79	62%	1.23	1.00	.092
$DAVNO_2$	.75	57%	.81	.52	.033

2. Estimation of the Hydrocarbon Effect

$$\left.\begin{array}{c} DPKNO_2 \\ \text{or} \\ DAVNO_2 \end{array}\right. = (A + C_0) + B_1 \cdot NO_25 + INTNO \cdot (B_2' + C_1 \cdot RATIO + C_2 \cdot NMHCPR)$$

	TOTAL CORR. COEF.	% VARIANCE EXPLAINED	$A + C_0$	B_1	B_2'	C_1	C_2
WINTER							
$DPKNO_2$	.77	60%	.93	.86	.15	*	*
$DAVNO_2$	.80	65%	.55	.48	.074	*	*
SUMMER							
$DPKNO_2$	.79	62%	1.23	1.00	.092	*	*
$DAVNO_2$	.75	57%	.81	.52	.033	*	*

*Not significant from zero at 95% confidence level.

Note: NMHCPR = .38[HC69 - 70 pphm]

Units of all variables are in pphm.

Table D-12 Summary of Nighttime Regressions for Houston/Mae

1. Regression of Nighttime NO_2 vs. NO_216, NITENO, and $O_3AFT \cdot NITENO$

$$\left.\begin{array}{c} NPKNO_2 \\ \text{or} \\ NAVNO_2 \end{array}\right\} = A + B_1 \cdot NO_216 + B_2 \cdot NITENO + B_3 \cdot NITENO \cdot O_3\ AFT$$

	TOTAL CORR. COEF.	% VARIANCE EXPLAINED	A	B_1	B_2	B_3
WINTER						
$NPKNO_2$	.77	60%	2.57	.43	*	.096
$NAVNO_2$	.76	57%	1.68	.27	-.11	.074
SUMMER						
$NPKNO_2$	.41	16%	3.00	.53	*	.039
$NAVNO_2$	.37	14%	1.74	.30	*	*

*Not significant from zero at 95% confidence level.

2. Dependence of Afternoon NO_2 (NO_216) on $NMHC/NO_x$ Ratio

WINTER: $NO_216 = 2.7\ \text{pphm}\ (1 - .010\ \frac{NMHCPR}{NOX69})$

SUMMER: $NO_216 = 2.4\ \text{pphm}\ (1 - .011\ \frac{NMHCPR}{NOX69})$

Note: Units of all variables are in pphm.

Table D-13 Summary of Daytime Regressions for Houston/Aldine

1. Regression of Daytime NO_2 vs. NO_25 and INTNO

$$\begin{matrix} DPKNO_2 \\ \text{or} \\ DAVNO_2 \end{matrix} = A + B_1 \cdot NO_25 + B_2 \cdot INTNO$$

	TOTAL CORR. COEF.	% VARIANCE EXPLAINED	A	B_1	B_2
WINTER					
$DPKNO_2$	.75	57%	.96	.68	.19
$DAVNO_2$	.70	49%	.52	.40	.050
SUMMER					
$DPKNO_2$	.67	45%	1.02	.50	.12
$DAVNO_2$	.67	45%	.41	.21	.080

2. Estimation of the Hydrocarbon Effect

$$\begin{matrix} DPKNO_2 \\ \text{or} \\ DAVNO_2 \end{matrix} = (A + C_0) + B_1 \cdot NO_25 + INTNO \cdot (B_2' + C_1 \cdot RATIO + C_2 \cdot NMHCPR)$$

	TOTAL CORR. COEF.	% VARIANCE EXPLAINED	A + C_0	B_1	B_2'	C_1	C_2
WINTER							
$DPKNO_2$	.75	57%	.96	.68	.19	*	*
$DAVNO_2$	.70	49%	.52	.40	.050	*	*
SUMMER							
$DPKNO_2$	.67	45%	1.02	.50	.12	*	*
$DAVNO_2$	.67	45%	.41	.21	.080	*	*

*Not significant from zero at 95% confidence level.

Note: NMHCPR = .5[HC - 133 pphm]

Units of all variables are in pphm.

Table D-14 Summary of Nighttime Regressions for Houston/Aldine

1. Regression of Nighttime NO_2 vs. $NO_2 16$, NITENO, and $O_3AFT \cdot NITENO$

$$\begin{matrix} NPKNO_2 \\ \text{or} \\ NAVNO_2 \end{matrix} = A + B_1 \cdot NO_2 16 + B_2 \cdot NITENO + B_3 \cdot NITENO \cdot O_3\ AFT$$

	TOTAL CORR. COEF.	% VARIANCE EXPLAINED	A	B_1	B_2	B_3
WINTER						
$NPKNO_2$	.59	34%	2.82	*	*	.119
$NAVNO_2$	.56	32%	1.78	*	-.28	.090
SUMMER						
$NPKNO_2$	*	*	*	*	*	*
$NAVNO_2$	*	*	*	*	*	*

*Not significant from zero at 95% confidence level.

2. Dependence of Afternoon NO_2 ($NO_2 16$) on $NMHC/NO_x$ Ratio

WINTER: No significant relationship between $NO_2 16$ and NMHCPR/NOX69

SUMMER: No significant relationship between $NO_2 16$ and NMHCPR/NOX69

Note: Units of all variables are in pphm.